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Recalibration of the U.S. National Prototype Kilogram

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The U.S. national prototype kilogram, K20, and its check standard, K4, were recalibrated at the Bureau International des Poids et Mesures (BIPM). Both these kilograms are made of platinum-iridium alloy. Two additional kilograms, made of different alloys of stainless steel, were also included in the calibrations. The mass of K20 in 1889 was certified as being 1 kg–0.039 mg. Prior to the work reported below, K20 was most recently recalibrated at the BIPM in 1948 and certified as having a mass of 1 kg–0.019 mg. K4 had never been recalibrated. Its initial certification in 1889 stated its mass as 1 kg–0.075 mg. The work reported below establishes the new mass value of K20 as 1 kg–0.022 mg and that of K4 as 1 kg–0.106 mg. The new results are discussed in detail and an attempt is made to assess the long-term stability of the standards involved with a view toward assigning a realistic uncertainty to the measurements.

Key words: International System of Units; kilogram unit; mass; national prototype kilograms; platinum-iridium kilograms; stainless steel kilograms; standards of mass; Système International d'Unités.

1. Introduction

The International Prototype Kilogram (IPK), made of an alloy of 90% platinum and 10% iridium, is kept at the International Bureau of Weights and Measures, or Bureau International des Poids et Mesures (BIPM), in Sèvres, France. The mass of this single artifact defines the kilogram unit in the International System of Units (SI): "The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram" [1][1]. Thus, calibration of national standards in SI units implies traceability to the IPK.

The IPK is actually one of three nearly identical kilogram artifacts ordered in 1878 from Johnson, Matthey and Company of London. Four years later, 40 more replicas of the IPK were ordered; these eventually becoming the first national prototypes. The United States was allotted artifacts No. 4 and No. 20 from these 40. (It is customary to refer to the i^{th} national prototype as Ki. Thus NBS is in possession of national prototypes K4 and K20.) Since their receipt by the U.S. government, K20 has been considered the national standard and K4 the "check standard" by which the constancy of K20 is monitored.

The BIPM now stores six replica or check kilograms in the same vault along with the IPK. All seven are kept under the strict control of the International Committee for Weights and Measures (CIPM). A brief history of the IPK and its check standards through 1975 is contained in [2].

The establishment of long-term stability limits for the national prototypes is important—if only because of the

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[1] Numbers in brackets indicate literature references.

infrequency of international comparisons. For this reason, we have included a fairly detailed review of the calibration history of the U.S. prototypes as well as a complete report of their recalibration by the BIPM in 1984.

The mass calibration service of NBS uses nichrome working standards at the kilogram level. These have a density of about 8.4 g/cm^3, considerably lower than the 21.55 g/cm^3 of the prototypes. Calibration of a nickel-chrome or a stainless steel kilogram by comparison to a platinum-iridium prototype presents many additional problems. Because of the metrological importance of these problems, two stainless steel kilograms, designated CH-1 and D2, also were sent to BIPM for calibration. These results are also examined.

2. BIPM Working Standards

The IPK has remained locked in a strongbox at the BIPM since its last use in 1946. The use of it or of any of its six check standards, which reside in the same enclosure, requires special permission of the CIPM. For routine calibrations, the BIPM uses two prototype kilograms, K9 and K31. These are now compared, at about 5-year intervals, with K25—a prototype which is reserved for exceptional usage. The use of K25 can be authorized by the director of the BIPM—a procedure that is far simpler than the protocol for use of either the IPK or any of its six check standards. The last measurements made with any of the six check standards occurred in 1965. Since then, BIPM calibrations of mass have been based on the assumption of long-term stability of K25. At 5-year periods, K25 has been cleaned and then used to recalibrate, K9 and K31.

The calibration history of K9 and K31 is shown in figure 1. Working standards K9 and K31 are each assigned an uncertainty at a level of one standard deviation of 8 μg [3]. Their present mass values and uncertainties result from the following chain:

Measurements	Year
K31 and K9 against K25	1983
K25 against two IPK check standards	1965
IPK check standards against the IPK	1946

The 1983 measurements were performed using the NBS-2 balance (see sec. 5.1) and thus are assigned a

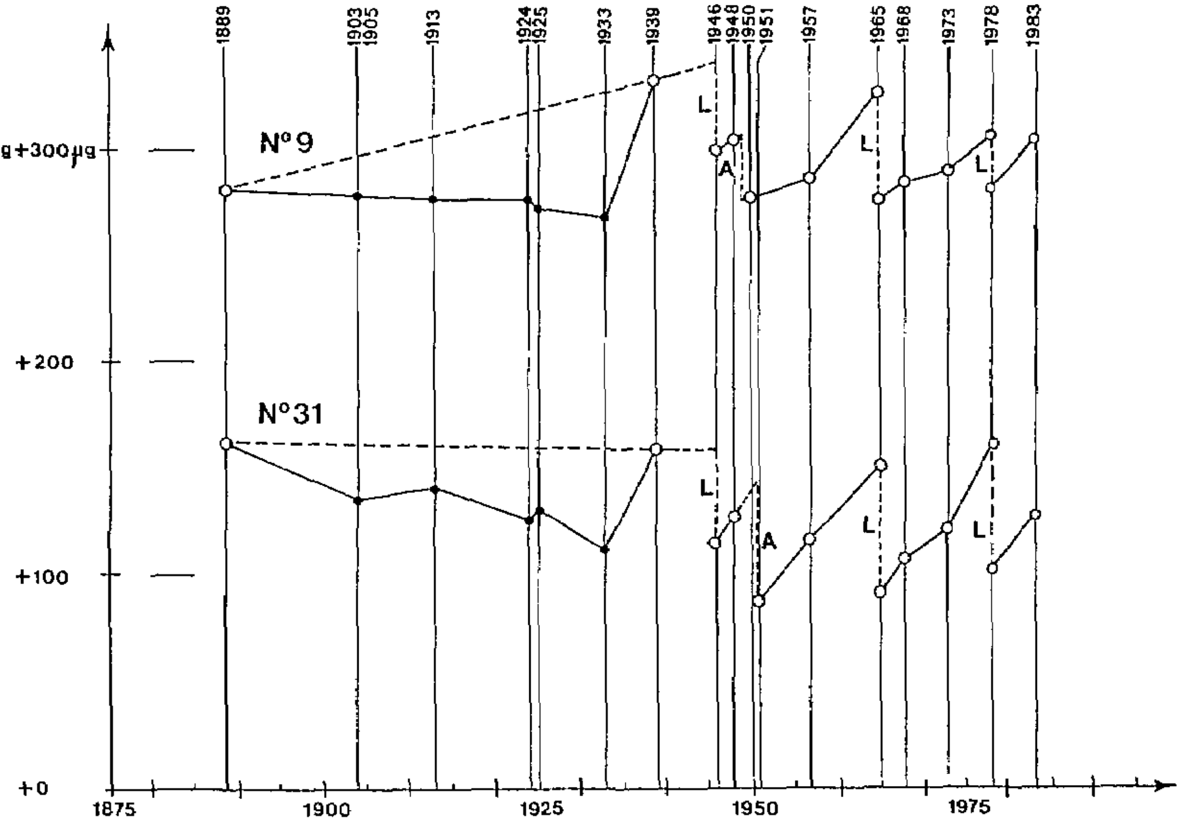

Figure 1–Calibration history of prototypes 9 and 31. The filled circles represent measurements which are tied less directly to the IPK than the open circles. Cleanings according to the method of Bonhoure [4] are indicated by "L." Two accidents are labeled "A." This graph, which extends the graph published in [2], was kindly supplied to us by the BIPM.

standard deviation of 1 μg. Measurements prior to 1970 were made primarily on a Rueprecht balance with a standard deviation for a single measurement of about 10 micrograms. Since the adoption of the cleaning method described by Bonhoure in 1946 [4], the long-term behavior of K9 and K31 has been easily interpreted: 1) the two accidents involved an appreciable loss in mass; 2) both prototypes show a mass increase with time if they are not cleaned (relative to K25 which was cleaned prior to the comparisons); 3) K31 has a tendency to pick up pollutants more quickly than K9 (the scratched surfaces of K31 make it a better trap for airborne particles [5]); and 4) cleaning the prototypes restores their mass to within 10 μg of their prior "clean" values.

3. Plan for BIPM Calibration of NBS Artifacts

Four one-kilogram artifacts were hand-carried from NBS, Gaithersburg to BIPM. The transatlantic crossings were made on commercial airlines. The artifacts were stored in the passenger section of the aircraft. Two of the artifacts, K4 and K20, are the national prototypes belonging to the United States. The other two, CH-1 and D2, are made of stainless steel. A detailed description of the artifacts used is given in section 4.

The carrying container for K20 was essentially that described in [6]. In this type of enclosure, the kilogram is held firmly on the top and bottom and is also clamped gently at three places around the side. All clamp faces conform to the contour of the adjacent kilogram surface. The clamped areas of the kilogram are protected by low-abrasive tissue paper which is backed by chamois skin, the latter having been previously degreased through successive soakings in benzene and ethanol. The outer case of the container is metal. The seal is not airtight.

The carrying case for K4 was of simpler design. The artifact was completely wrapped in tissue, then wrapped in chamois skin, and finally placed in a snugly-fitting brass container. Again, the container seal was not airtight.

Both stainless steel kilograms were wrapped in tissue paper and were then padded with successive layers of cotton batting and soft polyethylene foam. The outer container was a stiff cardboard tube. The padding held the kilogram fast within the tube.

After their arrival at BIPM at the beginning of December, 1983, all the artifacts were unpacked and stored in the mass laboratory. In February 1984 they were all calibrated twice against the BIPM working standards, K9 and K31. The first calibration was made without cleaning any of the artifacts. Before the second calibration, K20 and K4 were cleaned in the prescribed manner—wiped with benzene-soaked chamois skin, wiped with ethanol-soaked chamois skin, and then cleaned with steam from bi-distilled tap-water [4]. Except for steaming, the stainless steel artifacts underwent an identical cleaning procedure prior to the second calibration.

4. Description and History of Mass Standards Used

4.1 National Prototype K20 and K4

The manufacture of K20 and K4 has been well documented [6]. Such prototypes are replicas of the IPK. They are made of an alloy of 90% platinum and 10% iridium. At the time of manufacture, the ingots were swaged until their density reached a maximum, then formed into right-circular cylinders (height = diameter = 39 mm), and polished to a "rather handsome, but not specular" finish [7]. The edges of each prototype are slightly chamfered and each unit is identified with a number which is delineated by a slight change in the surface finish. The number is located on the side of the cylinder.

The surfaces of all the prototypes were carefully examined at the time of manufacture. The final step of polishing was done with emery which left the surface with a regular pattern of shallow marks. (Measurements on K22 reported in 1960 give a mean depth of 2 μm to these marks [8]). Occasionally small pits (*piqûres*) with a maximum diameter of 0.1 mm were noticed on the finished surfaces. K20 was found to have two such pits on its top and some striation marks in a small area on its base. The center of K4's top surface was found to have a dull finish and striations were noted in another small area of the top.

The surface of K20 has remained nearly as initially described. However, an NBS notebook entry of December 5, 1947 remarks that "K4 has numerous scratches on top and bottom and a black spot 15/32" [11.9 mm] from the bottom almost opposite the '4'." There is no indication of how or when K4 suffered this change in appearance, which persists.

Inspection of K4 after a cleaning in December 1971 revealed "two scratches on the top that appeared to be new." (See Appendix.)

The 1889 certificate listed the following properties for the U.S. national prototypes [6].

	Mass	Volume[2] at 0 °C
K20	1 kg − 0.039 mg	46.4030 cm^3
K4	1 kg − 0.075 mg	46.4296 cm^3

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[2] The volume in the original certificate was specified in milliliters. These numbers were converted to cubic centimeters by using the relation 1 ml = 1.000028 cm^3.

With a coefficient of volume expansion to a temperature t(°C) of [3]:

$$\alpha = (25.859 + 0.0065t) \times 10^{-6}/°\mathrm{C}$$

The expansion is assumed the same for all prototypes.

The standard deviation assigned to the measured masses was 3.3 μg (we have inferred this from the reported probable error of 2.2 μg). Measurements were made on balances having a standard deviation of 10 μg and results were solved by the method of least squares. No additional sources of error are mentioned. The fact that all artifacts were virtually identical in their physical properties undoubtedly minimizes or eliminates most errors of a nonstatistical nature (but see 5.1.3 below). The standard deviations for the volume assignments to K4 and K20 may again be inferred from the probable errors listed, i.e., 0.00010 cm^3 and 0.00028 cm^3. It was, however, recognized that in the case of hydrostatic volume measurements, many nonstatistical sources of error intervene. These sources are given in [9] along with a description of the pains taken to eliminate their effects.

After their initial calibration, artifacts K4 and K20 were shipped to the U.S. on separate vessels. K20 arrived first and was received with sufficient bureaucratic pomp to secure its status as the primary standard of mass in the U.S., K4 being henceforth treated as a check standard [10].

The U.S. artifacts were transferred to NBS soon after its establishment.

Prior to the work reported below, K20 was returned twice to BIPM—in 1937 and 1948. There was to have been the second reverification of all national prototypes in 1939 (the first occurred in 1899–1900; the U.S. did not participate). It is possible that K20 was sent to BIPM in 1937 as part of this planned exercise. At any rate, the deteriorating international situation put an end to the reverification plans. K20 was returned to NBS in 1938 with only a preliminary calibration certificate. After World War II, the results of this measurement were stated to be: mass of K20 = 1 kg–0.021 mg. The standard deviation of the result was thought to be an insignificant contribution to the total uncertainty of about 20 μg. The total uncertainty was based on experience with other prototypes which had been recalibrated.

The second periodic reverification was carried out in 1948–54, and K20 was again sent to BIPM for a portion of 1948. Measurements were made using K32 and K43, check standards of the IPK, as working standards. These check standards had been compared directly to the IPK in 1946 [11]. The result of this work showed the mass of K20 to be 1 kg–0.019 mg.

Although K4 had never been returned to BIPM, it was used several times at NBS in its role as check standard to K20. The results are summarized in table 1, which also includes the results of the newest comparisons. The implications of this table for long-term stability of K4 and K20 are discussed in the Appendix.

4.2 K650

In order to ascertain whether the artifacts sent to BIPM for calibration were in some way altered by their travel, it was essential to have at least one platinum-iridium artifact at NBS which could remain as a check standard. This was graciously provided by BIPM in the form of K650. This is one of a new series of prototypes

Table 1

Year	K20	K20-K4	Comments
1889	1 kg−0.039 mg	0.036 mg	BIPM, cleaned with alcohol and water vapors
1922		0.036	NBS, not cleaned
1937		0.05	NBS, prior to shipment to BIPM
1937	1 kg−0.021 mg		BIPM, wiped clean
1938		0.039	NBS, subsequent to return from BIPM
1947		0.045	NBS, prior to shipment to BIPM
1948	1 kg−0.019 mg		BIPM
1949		0.011	NBS, after return from BIPM
1970		0.058	NBS, measurements made on NBS-2
1971		0.038	NBS
1972		0.066	NBS
1983		0.072	NBS, prior to shipment to BIPM
1984	1 kg−0.001 mg	0.074	BIPM, as received
1984	1 kg−0.022 mg	0.084	BIPM, after cleaning
1984		0.075	NBS, after return from BIPM (as received)
1984		0.081	NBS, after cleaning

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[3] This number was modified to $(25.863-0.00562t)\times 10^{-6}/°\mathrm{C}$ in the 1947 certificate.

which is being manufactured by diamond turning [12], a machining process that leaves the surface of the kilogram in no need of polishing. As K650 was an early attempt, and the difficult task of machining to mass tolerance was not yet perfected, the finished mass of K650 was some 2 mg too small. This rendered it unsuitable for service as a national prototype but ideal for our purposes.

Its characteristics were described as follows:

Mass	Volume at 0 °C
1 kg−2.256 mg	46.4352 cm^3

with a coefficient of volume expansion,

$$\alpha=(25.863+0.00562t)\times 10^{-6}/°\mathrm{C}.$$

The artifact was received by NBS in good condition. Prior to its first use, however, a wide, shallow scratch was noticed on its basal surface. This damage was thought to invalidate its mass assignment; however, later recalibration at BIPM showed no significant decrease in mass (see results below). The artifact was returned to BIPM in October 1984.

4.3 KA

A second kilogram was also used as a check standard at NBS during the recent measurements. This artifact has belonged to the U.S. since 1821. It is designated KA and has been referred to as the "Arago kilogram" because its original certificate bore the surname of Dominique-Francois Arago, the 19th century scientist and liberal statesman. Its shape is a cylinder of minimum surface (i.e., height equal to diameter).

This artifact was manufactured from platinum sponge. Its density (20.8863 g/cm^3 at 20 °C) is about 2.6% below theoretical and its surface shows a great deal of pitting. The mass of this artifact is demonstratably unstable, decreasing monotonically with time, as can be seen in table 2. In this respect, its behavior is identical to other old platinum weights of similar manufacture—the British pound standards and the so-called Kilogram of the Archives [11], for example. But, while KA is unsuitable as a long-term standard, its short-term stability is sufficient for its use as a second check standard.

Table 2

Year	Mass of KA
1888	1 kg−4.63 mg
1922	1 kg−4.753 mg
1970	1 kg−4.803 mg
1984	1 kg−4.845 mg

4.4 D2, CH-1

Two stainless steel artifacts were also used in the comparisons with BIPM. These are designated D2 and CH-1. They are single-piece weights which are roughly cylindrical in shape except for a lifting knob on the upper surface. The bases of both weights are relieved so that each weight rests on a narrow annular area whose outer diameter is that of the weight itself. Their important physical properties are:

Weight	Nominal Mass	Volume at 20 °C	Coefficient of Expansion
D2	1 kg+13.49 mg	127.6250 cm^3	$45\times 10^{-6}/°C$
CH-1	1 kg−0.36 mg	124.9681 cm^3	$45\times 10^{-6}/°C$

D2 was manufactured by the Troemner Company of Philadelphia from an austenitic alloy similar to 18-8 stainless steel. D2 has been used extensively in calibration and research work at NBS for the last 15 years.

CH-1 was acquired from the Chyo Company of Kyoto, Japan in 1983. It was manufactured from an austentic stainless steel alloy having the following composition: 25.1% Ni, 29.9% Cr, 2.2% Mo, 1.45% Mn, 0.53% Si, 0.2% Cu, 0.07% C, 0.019% P. The metal was vacuum melted before being machined.

The volumes of both weights were determined at NBS at a temperature of 23 °C using distilled water as the standard. The uncertainty in the volume determination is calculated to be 5 ppm.

The volumetric thermal expansion of D2 near room temperature was supplied by the manufacturer. The volume expansion of CH-1 was determined by linear expansion measurements at NBS made on a sample rod supplied by the manufacturer.

5. Principles of Mass Comparisons

5.1 Description and Function of an Ideal Balance

The balances used in the recent mass comparisons were: NBS-2, a single-pan balance designed and built at NBS and then permanently transferred to BIPM in 1970 [13]; and V-1, the primary kilogram comparator of NBS, manufactured by the Voland Corporation of Hawthorne, NY. Both balances are similar in design and are based on design principles established by NBS researchers during the 1960's [14,15].

The major design features of these balances are well known [13]. Weights are manipulated on or off the pan remotely by the proper combination of raising, lowering, and rotation of a weight table. Comparisons of two weights are done by substitution on the single pan, often referred to as Borda's method. Both balances are free-swinging so that the equilibrium position of the beam must be inferred from brief observations of the beam oscillations. At both BIPM and NBS, these observations consist of recording successive turning points of the swinging beam. These points are at present determined by reading an optical scale, the image of which is projected from a mirror fixed to the balance beam. At NBS, five successive turning points are read. The beam amplitude is always adjusted to 2 mg±0.04 mg (peak to peak). Since the beam has a period of about 30 s, this means that the beam swings freely for 1-1/2 min for each determination of an equilibrium position. The beam is first stopped using a braking mechanism at an angle corresponding to 2 mg below equilibrium. The brake is then released and readings commence after one complete oscillation. The first turning point is taken on the same side of the equilibrium position for every measurement. If the five turning points read are $l_1, l_2, \ldots, l_5$, we infer the rest point λ from the relation

$$\lambda=(1/12)(2l_1+3l_2+2l_3+3l_4+2l_5). \qquad (1)$$

Bignell has recently discussed the advantages of eq (1) over other possible formulas [16]. For our measurements, we may use Bignell's results to show that eq (1) leads to a bias in λ of approximately 0.01 μg. This bias will be constant to 2%. It is thus negligible.

A very important feature of these balances is the inclusion of a constant-load stop which maintains all but about 20 mg of the full 1-kg load on the beam, its knives and its bearings, through the exchange of weights. This feature, which causes the balance behavior to better approximate ideality, has been discussed in great detail elsewhere [15].

Differences in balance equilibrium position ideally correspond to different forces on the pan. In order to relate observed differences in beam angle to differences in force (or mass) it is necessary to determine the balance sensitivity. This is accomplished by the addition of a small sensitivity weight s (2 mg at NBS). The mass and volume of this weight must be known sufficiently well so that the apparent mass which it adds to the balance pan is determined to ~0.5 μg. In determining the mass of the sensitivity weight from a calibration chain starting from 1-kg standards, the kilogram standards need only be known to ±0.25 g (i.e., 1 part in 4000), a tolerance which is never in doubt.

When one considers that the ratio of the beam arms of the balance ideally should be constant to 1×10^{-9} (i.e., a differential change in length of less than 0.075 nm for V-1), it is not surprising that successive equilibrium readings of a single weight often increase or decrease monotonically for long periods of time. This could be due, for instance, to a very slight differential heating of the two ends of the brass beam ($\Delta T=56$ μK would be sufficient). A change in balance equilibrium for successive observations of the same weight will be referred to as balance drift.

In order to take account of linear drifts, as well as to measure the balance sensitivity, the following double substitution involving five equilibrium observations is used to determine the difference in apparent mass[4] between an object A and and an object B:

Observation	Balance Equilibrium Value	Object on Balance Pan
1	λ_1	A
2	λ_2	B
3	λ_3	B+s
4	λ_4	A+s
5	λ_5	A

The apparent mass difference between A and B, $P(\mathrm{A}-\mathrm{B})$ is then estimated by

$$P(\mathrm{A}-\mathrm{B})=\frac{\lambda_1-\lambda_2-\lambda_3-\lambda_4}{-\lambda_2+\lambda_3+\lambda_4-\lambda_5}\quad P(\mathrm{s}), \qquad (2)$$

where $P(\mathrm{s})=m_\mathrm{s}-\rho v_\mathrm{s}$, ρ is the averge air density during the double substitution and v_s is the volume of s.

Using eq (2) to estimate $P(\mathrm{A}-\mathrm{B})$ serves to eliminate the effect of a linear drift in time of the equilibrium value of the balance. In fact, it has been pointed out [53] that the right-hand side (r.h.s.) of (2) provides an unbiased estimate for $P(\mathrm{A}-\mathrm{B})$ with no statistical degrees of freedom, provided only that the drift between observations 1 and 2 equals that between observations 3 and 4, and the drift between observations 2 and 3 equals that between observations 4 and 5. This may be a better model of reality than a simple linear drift because the drift which occurs when kilogram artifacts are exchanged on the balance pan may differ from that which occurs when only s is added or subtracted (although even in the latter case, the kilogram weight is removed from the pan and then replaced).

The standard deviation of measurement of $P(\mathrm{A}-\mathrm{B})$ on V-1 is about 4 μg and about 1 μg on NBS-2.

In order to estimate the mass difference between A and B, $m_\mathrm{A}-m_\mathrm{B}$, from $P(\mathrm{A}-\mathrm{B})$, one must recognize that

$$m_\mathrm{A}-m_\mathrm{B}=P(\mathrm{A}-\mathrm{B})+\rho(V_\mathrm{A}-V_\mathrm{B})+f_1(\Delta\mathrm{s})+f_2(\Delta\mathrm{h}) \qquad (3)$$

where V_A and B_B are the volumes of A and B, f_1 is a function of the difference in surface of A and B and f_2 is

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[4] By "apparent mass" we mean the force introduced by adding an object to the balance pan divided by the gravitational acceleration at the center of mass of the added object.

a function of the difference in centers of mass of A and B. The functions f_1 and f_2 are often neglected although, for many conditions, are not really negligible. Their effects will be mentioned below. For the moment, we will estimate m_A-m_B by the relation

$$m_A-m_B=\frac{\lambda_1-\lambda_2-\lambda_3+\lambda_4}{-\lambda_2+\lambda_3+\lambda_4-\lambda_5}(m_s-\rho V_s) +\rho(V_A-V_B). \tag{4}$$

The determination of m_A-m_B by eq (4) has no statistical degrees of freedom. In order to provide a good statistical check, four weights, A, B, C, and D, are usually intercompared in all six possible pairings: A−B, A−C, A−D, B−C, B−D, C−D. This can be thought of as a weighing "design" composed of six subweighings. If the mass of one of these weights, for example A, is known, the mass of the others can be determined by least squares fitting to the data [17]. If m_B, for example, is also known, the least squares estimate of m_B can be compared to the accepted value, thus providing the means for a t-test [18].

5.2 Non-Ideal Behavior

The V-1 and NBS-2 balances do not behave in the ideal way described above. Thus the method of calibrating unknown masses must be altered from the simple algorithm just outlined. We now discuss the necessary modifications.

5.2.1 Pressure Drift: The NBS-2 balance is sealed against changes in the ambient barometric pressure. The V-1 balance, however, is not sealed. Thus changes in barometric pressure will affect that balance equilibrium during a double substitution if the volume of the weight on the pan differs significantly from the volume of the balance counter-weight. (Changes in temperature and relative humidity are insignificant for the times involved.) In order to eliminate this unwanted effect, the average barometric pressure during the 1-1/4 min needed to determine each λ_i is recorded. Then, λ_1, λ_3, λ_4 and λ_5 are corrected to the value they would have had at P_2, the pressure recorded for λ_2. The corrected value λ_i' is given by

$$\lambda_i'=\lambda_i+\frac{(P_i-P_2)(V_i-V_{cw})\rho}{P_2 \quad S}$$

where V_{cw} is the volume of the balance counter-weight, V_i is the volume of the weight on the balance pan, and ρ is now the air density at the time of the second observation, and S is the balance sensitivity (see sec. 5.2.2). The ratio of the balance arms is assumed equal to 1 to within 4%. When stainless steel and platinum weights are used in the same weighing design, the magnitude of $\lambda_i'-\lambda_i$ can reach 15 μg.

5.2.2 Sensitivity: Every subweighting includes an estimate of the current balance sensitivity,

$$S=\frac{m_s-\rho V_s}{-\lambda_2+\lambda_3+\lambda_4-\lambda_5}.$$

In the course of a complete weighing design, which requires some 150 min, the sensitivity is seen to decrease by about 0.2%. This is true of both NBS-2 and V-1. The sensitivity recovers when the balance is fully arrested for several hours (i.e., knives and flats separated). The decrease in sensitivity was noted in the paper reporting the construction of NBS-2 [13]. At that time, the author speculated that elastic deformation of the metal knives could account for the observed behavior. In our view, this remains a viable hypothesis. The effective radii of the knives are ~20 μm which is the same order of magnitude as the distance between the center of curvature of the main knife and the center of mass of the balance beam. The latter distance largely determines balance sensitivity [19].

Since the decrease in balance sensitivity during a series is slow and monotonic, it has no serious consequences. The observed decrease in sensitivity simply underlines the necessity of using an algorithm which measures balance sensitivity for each subweighing.

5.2.3 Bias: In order to use a least squares approach to the solution of a weighing design, it is necessary that the r.h.s. of eq (4) be an unbiased estimator of m_A-m_B. For both NBS-2 and V-1, this assumption has been found to be violated. A detailed account of the problem as regards NBS-2 is found in [53].

For V-1 we have found that the usual subweighing involving any two weights A and B gives a biased estimate of m_A-m_B. That is, instead of eq (4), we find that

$$\delta_{A,B}\equiv\epsilon+m_A-m_B=\frac{\lambda_1-\lambda_2-\lambda_3+\lambda_4}{-\lambda_2+\lambda_3+\lambda_4-\lambda_5}. \tag{4}$$

The additional term, ϵ, seems independent of which subweighing of the design is involved, although we cannot be definitive on this point. This is a somewhat different outcome from that described for NBS-2 in [53]. We have found that ϵ is about +2.4 μg with a mean standard deviation of 0.4 μg (22 degrees of freedom).[5]

We have essentially adopted the approach taken by BIPM for dealing with this bias (see [53]). As the authors

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[5] It may be of historical interest to point out that unexplained systematic behavior has been reported before for a two-pan balance [30]. In that case, a change in procedure removed the problem.

of this reference point out, although the bias cannot yet be satisfactorily explained, its effect can, nevertheless, be eliminated. This is done by duplicating all the subweighing in a design on the succeeding day, the only change being that all weighings are reversed:

Design for Day 1	**Design for Day 2**
A−B	B−A
A−C	C−A
A−D	D−A
B−C	C−B
B−D	D−B
C−D	D−C

Then for each pair of weights x and z,

$$(\delta_{x,z}-\delta_{z,x})/2$$

is now an unbiased estimator for $m_x - m_z$. The quantity $(\delta_{x,z}+\delta_{z,x})/2$ gives an estimate for ϵ.[6]

Six weights were involved in the measurements at NBS—K20, K4, KA, K650, CH-1, and D2. Six weights were also involved in the measurements at BIPM—K9, K31, K20, K4, CH-1, and D2. These were measured in three separate groupings. In the case of NBS, the scheme shown in table 3 was carried out over a period of 8 days. Unlike NBS-2, balance V-1 can only accommodate four weights on its remote-controlled weight changer. Therefore, in the case of V-1, the balance needed to be opened after Days 2 and 5. After opening, the balance required a full day to re-equilibrate.

The design of table 4 provides 18 unbiased estimates of mass differences among pairings of the six weights. The least squares solution as well as the variance-covariance matrix are readily found for the restraint that the mass of K20 is known. These matrices are also shown in table 4.

6. Necessary Corrections

6.1 Added Weights

Kilogram balances such as NBS-2 and V-1 have a very narrow on-scale range—typically 40 mg. There are reasons, however, why it is imprudent to operate the balance over its full range. First, the scale may be nonlinear. This could occur, for instance, if one of the two knives had an effective radius which was a function of beam angle [21]. Second, the balance reading is more immune to vibrational noise if the beam is maintained nearly horizontal [19].

In order to minimize unwanted effects, the following steps are taken: 1) The amplitude of the beam swing is always adjusted to be the same for each measurement—in our case, 4 mg peak-to-peak, and 2) small weights are added to the kilogram artifacts as needed so that the four artifacts agree in apparent mass to within 1 mg. These precautions ensure that the five observations of a subweighing are all derived from roughly the same place on the knife-edge profiles.

In the case of comparing platinum-iridium prototypes to D2 and CH-1, as much as 95 mg must be added to the stainless steel artifacts to bring their apparent masses to within the 1-mg tolerance. Obviously the masses and volumes of the added weights must be known with sufficient accuracy (i.e., about 1 μg and 1 mm^3) so that the final mass assignments are not compromised.

Calibration of the added weights is similar to the problem of calibration of the sensitivity weight and is similarly resolved. We must work down in a calibration chain from 1 kg to 1 mg and we must have a resulting inaccuracy to no worse than 1 μg in 95 mg (11×10^{-6}). Thus at the outset we must know the value of the 1-kg standards to 0.011 g. This is no problem. As in the case of the sensitivity weight, the calibration accuracy is limited primarily by the ratio of precision-to-load of the balances used in the calibration chain. Typical results are shown in table 5. The uncertainties are correlated because of the weighing design which was used [17].

Table 3

Day 1	Day 2	Day 4	Day 5	Day 7	Day 8
K20,K4	K4,K20	KA,K650	K650,KA	CH-1,D2	D2,CH-1
K20,KA	KA,K20	KA,CH-1	CH-1,KA	CH-1,K20	K20,CH-1
K20,K650	K650,K20	KA,D2	D2,KA	CH-1,K4	K4,CH-1
K4,KA	KA,K4	K650,CH-1	CH-1,K650	D2,K20	K20,D2
K4,K650	K650,K4	K650,D2	D2,K650	K2,K4	K4,D2
KA,K650	K650,KA	CH-1,D2	CH-1,D2	K20,K4	K4,K20

---

[6] In [53], a design is advocated which requires rotation of the weight table between sucessive subweighings. We have not, for technical reasons, used the BIPM design but have, instead, rotated the weight table ±1/8 revolution between consecutive subweighings involving the same weight for the first observations.

Table 4. The matrix of observations, variance-covariance matrix, and transpose of the solution matrix [17]. The value for each observed difference is derived from a weighing and its opposed weighing as explained in section 5.1.3 and [53]. It is assumed that the mass of K20 is known.

			Matrix of observations			
			Wt			
Obs #	K20	K4	KA	K650	CH-1	D2
1	1	−1	0	0	0	0
2	1	0	−1	0	0	0
3	1	0	0	−1	0	0
4	0	1	−1	0	0	0
5	0	1	0	−1	0	0
6	0	0	1	−1	0	0
7	0	0	1	1	0	0
8	0	0	1	0	−1	0
9	0	0	1	0	0	−1
10	0	0	0	1	−1	0
11	0	0	0	1	0	−1
12	0	0	0	0	1	−1
13	0	0	0	0	1	−1
14	−1	0	0	0	1	0
15	0	−1	0	0	1	0
16	−1	0	0	0	0	1
17	0	−1	0	0	0	1
18	1	−1	0	0	0	0
Restraint	1	0	0	0	0	0
Variance-covariance matrix:						
	0	0	0	0	0	0
	0	2500	1250	1250	1250	1250
(1/10000)x	0	1250	2917	1667	1458	1458
	0	1250	1667	2917	1458	1458
	0	1250	1458	1458	2917	1667
	0	1250	1458	1458	2667	2917
Transpose of solution matrix:						
	0	−2500	−1250	−1250	−1250	−1250
	0	−1250	−2917	−1667	−1458	−1458
	0	−1250	−1667	−2917	−1458	−1458
	0	1250	−1667	− 417	− 208	− 208
	0	1250	− 417	−1167	− 208	− 208
	0	0	1250	−1250	0	0
	0	0	1250	−1250	0	0
	0	0	1458	208	−1458	− 208
(1/10000)x	0	0	1458	208	− 208	−1458
	0	0	208	1458	−1458	− 208
	0	0	208	1458	−208	−1458
	0	0	0	0	1250	−1250
	0	0	0	1250	1250	−1250
	0	1250	1458	1458	2917	1667
	0	−1250	208	208	1667	417
	0	1250	1458	1458	1667	2917
	0	1250	208	208	417	1667
	0	−2500	−1250	−1250	−1250	−1250

6.2 Air Buoyancy

Additional weights were necessary to bring the apparent mass of a stainless steel kilogram standard into near equality with a platinum-iridium prototype, i.e.,

$$|P(\mathrm{K}-[\mathrm{R}+\Sigma\mathrm{W}])|<1\ \mathrm{mg}$$

where K is made of platinum-iridium, R is made of stainless steel and ΣW represents a summation of small weights whose mass is nominally 95 mg.

However, the quantity of interest is $m_\mathrm{K}-m_\mathrm{R}$:

$$m_\mathrm{K}-m_\mathrm{R}=P(\mathrm{K}-[\mathrm{R}+\Sigma\mathrm{W}])+m_{\Sigma\mathrm{W}}-\rho(V_\mathrm{R}-V_\mathrm{K})-\rho V_{\Sigma\mathrm{W}}+f_1+f_2. \quad (5)$$

The term $\rho(V_\mathrm{R}-V_\mathrm{K})$ is approximately equal to $m_{\Sigma\mathrm{W}}$.

Table 5. Typical calibration values for a set of fractional weights. The uncertainties are given at a level of 1 standard deviation according to [31]. The uncertainty is virtually all statistical in nature (Type A). The results are correlated so that, for example, the uncertainty in the combination of (50 mg + 30 mg + 10 mg) is 0.27 μg.

Nominal Mass (mg)	Correction (mg)	Uncertainty (μg)	Vol. at 20 °C (cm^3)	Coef. of Exp. (10^{-6}/°C)
50	−0.02936	0.23	0.00301	20
30	−0.01361	0.19	0.00181	20
20	−0.02715	0.15	0.00740	69
10	−0.02037	0.18	0.00370	69
5	−0.01514	0.15	0.00185	69
3	−0.02223	0.16	0.00110	69
2	+0.00971	0.14	0.00074	69
1	+0.03106	0.18	0.00038	69

Clearly, if ρ were zero, neither the added mass $m_{\Sigma W}$ nor the buoyancy correction $-\rho(V_R - V_K)$ would be necessary. Performing the required mass comparisons under vacuum conditions presents a number of as yet unstudied problems, however; mass stability and balance performance are chief among them. As a related problem, one would have to re-open the question of whether the SI definition of the kilogram ought to be the mass of the IPK in equilibrium with laboratory air or in vacuum. These concerns have potential interest but are beyond the scope of this report.

A brief word should be said about the reliance of the necessary buoyancy corrections on SI units of mass. The density D_x of a weight x is defined as $D_x \equiv m_x/V_x$. Quantities such as $m_x - \rho V_x$ which occur in weighing equations can equally be written $m_x(1-\rho/D_x)$. Thus, for instance, instead of estimating m_R by

$$m_R = -P(K-R) + m_K + \rho(V_R - V_K)$$

we can, equally, write

$$m_R = \frac{-P(K-R) + m_K(1-\rho/D_K)}{1-\rho/D_R}.$$

In the latter formulation, it becomes clear that buoyancy corrections only involve density ratios (ρ/D_K and ρ/D_R) and therefore are fundamentally independent of which consistent system of units is employed. One can, in fact, easily conceive of experiments to measure the densities of ρ and D relative to the density of some natural standard—distilled water, for instance. Such experiments usually involve weighing but the instrument used need only be a linear force transducer—the proportionality constant between transducer reading and SI units need not be known. This approach relies on the suitability of water as a density reference for laboratories separated by large distances. Recently, renewed interest in water suggests that distilled tap water at a given temperature is probably uniform in major metrology laboratories to at least 10×10^{-6} [22].

Although improvements in establishing reference densities in SI units through solid objects have lowered uncertainties by an order of magnitude [23], this has been an iterative procedure which relied in part on the soundness of the mass unit. The mass unit was able to be established and disseminated through the national prototypes to the required precision because distilled water, for all its shortcomings, was a sufficiently good density reference.

6.2.1 Densities of Mass Artifacts: Since the density of artifact standards is stable, an error in the density (or volume) assignment to a mass standard propagates as an error which is systematic to all future measurements. The magnitude of the error incurred is $(\rho_1 - \rho_2)\delta V_x$, where δV_x is the error in the volume assigned to a mass artifact x, ρ_1 is the air density at the time of calibration of x and ρ_2 is the air density of the time of subsequent use of x. This means that although the error in assignment of an SI mass value to x may be large (i.e., $\rho_1 \delta V_x$), x can nevertheless be used without significant error to propagate SI mass values to other weights provided that the subsequent calibrations are carried out at an air density ρ_2 sufficiently close to ρ_1.

6.2.2 Density of Air: Historically, the density of laboratory air has been determined from an equation of state involving temperature, pressure, and relative humidity. The equation was derived by making small corrections to the density of air under specified reference conditions near those normally encountered [24]. The reference density was determined relative to distilled water [25].

Recently, the equation of state has been rederived on a firmer theoretical basis. Also, refinements have been added—such as a correction for changes to the ambient levels of carbon dioxide [26]. This approach has won endorsement by the CIPM, which has recommended a specific formulation, "Formula for the Determination of the Density of Moist Air (1981)," for international work [27].

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the object in the hydrostatic bath may be 50 cm below the balance weights [40]. This, in fact, was the motivation for the early BIPM experiments.)

7. Results at BIPM

G. Girard, who performed the calibrations at BIPM, has summarized his results as follows:

In practice the comparisons were carried out in the following manner:

3 weighings:

K32	D2	CH-1	K4				
		CH-1	K4	K20	K9		
				K20	K9	K31	D2

Design of Weighing #1	
K31	D2
D2	CH-1
CH-1	K4
K4	K31
K31	CH-1
D2	K4

Design of the Opposed Weighing	
D2	K31
CH-1	D2
K4	CH-1
K31	K4
CH-1	K31
K4	D2

The mass value of the sensitivity weight used was last determined in September–October, 1983.

The four NBS standards were compared to the two platinum-iridium standards of BIPM, first in the state in which they arrived at BIPM, then after a cleaning in benzene and alcohol; prototypes K4 and K20 of platinum-iridium were, in addition, washed under a steam jet of doubly-distilled water.

These comparisons took place from January 30 to February 7, 1984 (group a, before cleaning-washing) and from February 23 to March 1, 1984 (group b, after cleaning-washing).

Correction for Air Buoyancy: The density of moist air, in the course of each weighing, was calculated with the aid of the "Formula for the determination of the density of most air (1981)" [24].

The different ambient parameters and the instruments used for their determination in the course of the two groups of measurements are the following:

Temperature: Rosemount platinum resistance thermometer and Automatic Systems Laboratories F17A alternating current bridge. The readings of this thermometer were verified, before the start of the measurements, by comparison to a Tinsley platinum resistance thermometer calibrated in the IPTS-68.

Uncertainty$\approx$2 mK

Mean temperatures (a) 20.27 °C
(b) 20.24 °C

Pressure: Ruska DDR-6000 calibrated by comparison with the BIPM interferential manobarometer before and after each group of measurements.

Uncertainty$\approx$2Pa

Average pressure (a) 100,922 Pa
(b) 101,015 Pa

Relative Humidity: Hygrodynamics transducer calibrated against an EG&G dewpoint hygrometer before and after the comparisons, at the ambient relative humidity.

Uncertainty$\approx$1%to 2%

Mean relative humidities (a) 41%
(b) 38%

CO$_2$: Ambient air near the balance is brought to an MSA analyser. This device is based on infrared absorption; the mole fraction of CO$_2$ in the air is measured before closing up the balance.

Uncertainty$\approx$0.0001

Mean mole fractions (a) 0.00041
(b) 0.00062

The mean values of air density in the two groups are, therefore,

(a) 1.194 40 mg/cm^3
(b) 1.195 91 mg/cm^3

After making corrections for gravitational gradient, the following results were obtained:

Before Cleaning	
K4	1 kg−0.075 mg
K20	−0.001 mg
CH-1	−0.377 mg
D2	+13.453 mg

The estimated standard deviation of each result is 1.2 μg.

After Cleaning	
K4	1 kg−0.106 mg
K20	−0.022 mg
CH-1	−0.384 mg
D2	+13.447 mg

The estimated standard deviation of each result is 1.3 μg.

Kilogram K650 was remeasured at BIPM in February 1985. The results are: mass=1 kg−2.264 mg; σ=0.5 μg [52].

8. Results at NBS

The 1984 results at NBS, carried out after the BIPM recalibration, will be presented in detail. The 1982 measurements will be summarized.

8.1 1984 NBS Measurements

Upon return to NBS, K20 and K4 were used in some preliminary measurements with KA and K650. K20 and K4 were then cleaned in benzene and ethanol after which they were washed in a vapor jet of distilled water. After cleaning, they were again compared with KA and K650. The results clearly show that K20 was un-

the object in the hydrostatic bath may be 50 cm below the balance weights [40]. This, in fact, was the motivation for the early BIPM experiments.)

7. Results at BIPM

G. Girard, who performed the calibrations at BIPM, has summarized his results as follows:

In practice the comparisons were carried out in the following manner:

3 weighings:

K32	D2	CH-1	K4				
		CH-1	K4	K20	K9		
				K20	K9	K31	D2

Design of Weighing #1		**Design of the Opposed Weighing**	
K31	D2	D2	K31
D2	CH-1	CH-1	D2
CH-1	K4	K4	CH-1
K4	K31	K31	K4
K31	CH-1	CH-1	K31
D2	K4	K4	D2

The mass value of the sensitivity weight used was last determined in September–October, 1983.

The four NBS standards were compared to the two platinum-iridium standards of BIPM, first in the state in which they arrived at BIPM, then after a cleaning in benzene and alcohol; prototypes K4 and K20 of platinum-iridium were, in addition, washed under a steam jet of doubly-distilled water.

These comparisons took place from January 30 to February 7, 1984 (group a, before cleaning-washing) and from February 23 to March 1, 1984 (group b, after cleaning-washing).

Correction for Air Buoyancy: The density of moist air, in the course of each weighing, was calculated with the aid of the "Formula for the determination of the density of most air (1981)" [24].

The different ambient parameters and the instruments used for their determination in the course of the two groups of measurements are the following:

Temperature: Rosemount platinum resistance thermometer and Automatic Systems Laboratories F17A alternating current bridge. The readings of this thermometer were verified, before the start of the measurements, by comparison to a Tinsley platinum resistance thermometer calibrated in the IPTS-68.

Uncertainty $\approx$ 2 mK
Mean temperatures (a) 20.27 °C
(b) 20.24 °C

Pressure: Ruska DDR-6000 calibrated by comparison with the BIPM interferential manobarometer before and after each group of measurements.
Uncertainty $\approx$ 2Pa
Average pressure (a) 100,922 Pa
(b) 101,015 Pa

Relative Humidity: Hygrodynamics transducer calibrated against an EG&G dewpoint hygrometer before and after the comparisons, at the ambient relative humidity.
Uncertainty $\approx$ 1%to 2%
Mean relative humidities (a) 41%
(b) 38%

CO_2: Ambient air near the balance is brought to an MSA analyser. This device is based on infrared absorption; the mole fraction of CO_2 in the air is measured before closing up the balance.
Uncertainty $\approx$ 0.0001
Mean mole fractions (a) 0.00041
(b) 0.00062

The mean values of air density in the two groups are, therefore,

(a) 1.194 40 mg/cm^3
(b) 1.195 91 mg/cm^3

After making corrections for gravitational gradient, the following results were obtained:

Before Cleaning		**After Cleaning**	
K4	1 kg − 0.075 mg	K4	1 kg − 0.106 mg
K20	−0.001 mg	K20	−0.022 mg
CH-1	−0.377 mg	CH-1	−0.384 mg
D2	+13.453 mg	D2	+13.447 mg

The estimated standard deviation of each result is 1.2 μg.

The estimated standard deviation of each result is 1.3 μg.

Kilogram K650 was remeasured at BIPM in February 1985. The results are: mass = 1 kg − 2.264 mg; σ = 0.5 μg [52].

8. Results at NBS

The 1984 results at NBS, carried out after the BIPM *recalibration, will be presented in detail. The 1982 mea*surements will be summarized.

8.1 1984 NBS Measurements

Upon return to NBS, K20 and K4 were used in some preliminary measurements with KA and K650. K20 and K4 were then cleaned in benzene and ethanol after which they were washed in a vapor jet of distilled water. After cleaning, they were again compared with KA and K650. The results clearly show that K20 was un-

These did not use the symmetrized algorithm shown in section 5.1.3. There are other differences as well. The most important of these is that, in 1983, the balance pan was loaded and all knife-flat bearings were engaged for 18 h prior to the start of measurements. In the BIPM measurements and in 1984 NBS measurements duplicating the BIPM algorthm, the balance is fully arrested until the time of use. At BIPM, the balance is "warmed up" by making three observations prior to the start of data taking. At NBS, warm-up consists of a practice observation of each of the four weights in the design.

Four designs were run using K20, K4, KA and K650. All the weights were rinsed in benzene, rinsed in ethanol, and washed with steam prior to the first and third measurements. The pooled standard deviation for these four runs was 4.5 μg (12 degrees of freedom). The mass of K20 given in the 1948 certificate was used to restrain the least squares solution. We therefore expect that the standard deviation of the derived masses of K4, KA and K650 will be $\sqrt{1/2}\cdot 4.5\ \mu\text{g}=3.2\ \mu\text{g}$. The pooled standard deviation of the six duplicate measurements made without cleaning is 2.9 μg. This agrees well with the least squares value and therefore does not indicate a "between times" component to the standard deviation [18].

One can also examine the results for changes which may have occurred upon cleaning. This is done by looking at the average values for K4, KA and K650 for measurements 1 and 2 as compared with measurements 3 and 4:

	K4	KA	K650
Average Difference	-8.7 μg	-1.9 μg	-9.4 μg
Expected SD of Difference		4.5 μg	

These results suggest that the cleaning procedures used may produce perceptible changes in the relative masses of platinum weights. Two rounds of measurements were carried using K20, K4 and various lower-density weights. K20 and K4 were recleaned before each round and used in five designs. The average differences for the two additional rounds as compared to the average of the first two measurements (1 and 2) is:

	(K4)	(K4)'
Average Differences	-3.8 μg	-4.0 μg
Expected SD of Difference	2.7 μg	

These last results are consistent with the *average* value of the first four measurements. Since the author had no experience cleaning kilogram prototypes, the progression of values shown above may represent a learning curve. The metrologist with the most experience in cleaning platinum-iridium prototypes is undoubtedly G. Girard of BIPM. Using NBS-2, he has demonstrated a cleaning stability of approximately 2 μg. (The data presented are for K63—measurements involved three complete cleaning cycles during a period of 8 months [32].)

The 1984 results at NBS may be compared with the 1983 results as shown in table 8a. We have assumed that KA and K650 have not changed in mass over the 16-month period. The difference in mass seen for K20 and K4 is consistent with what was observed at BIPM upon cleaning. We can, therefore, conclude that the cleaning administered to K4 and K20 at BIPM in 1984 was more thorough than that performed at NBS in 1983. The 6-μg discrepancy between the cleaning loss measured at BIPM and that inferred from measurements at NBS can be explained in at least three ways:

1) The 6-μg difference is barely significant given the combined standard deviations of the NBS (4.2 μg) and BIPM (1.4 μg) results.

2) KA and K650 may have picked up surface dirt during the intervening 16 months—about 2 μg/year seems typical for weights stored in a similar fashion [5].

3) The measurement scheme used in 1983 may give systematic differences from that used in 1984. To check this possibility, we performed several additional measurements involving K20, K4, KA and K650 using the 1983 measurement scheme. The results are shown in table 8b.

The comparisons of mass values found for CH-1 and D2 at NBS before and after the BIPM calibrations show closure to an average of 11.5 μg. This number does not include a correction to the same value of relative humidity for both sets of measurements—such a "correction" would worsen agreement by an additional 10 μg. The 1983 measurements at NBS were corrected for the recalibration of our humidity sensors in 1984 (see above). Also, in 1983 there were no background measurements of CO_2 fraction in the balance air. We estimate that these shortcomings increase the uncertainty of buoyancy corrections for the 1983 measurements by 8 μg over the 1984 NBS uncertainties.

We should add that D2 was measured against K20 in 1970. The measurements were made on NBS-2 at NBS. The 1948 calibration value of K20 was assumed. The results were:

$$\text{Mass of D2 (1970)} = 1\ \text{kg} + 13.521\ \text{mg}\ (6\ \mu\text{g})$$

where the 6 μg is the standard deviation of the mean of three measurements. The measurements were made at a relative humidity of about 21%. The 1970 data have

Table 8. In A, one sees that KA and K650 give self-consistent results. One may infer that K20 and K4 have lost mass after leaving NBS in 1983. In B, one may note the effect of a change in measurement algorithm. The conclusions found in A are still intact, but the quantitative mass losses now agree better with cleaning losses observed at BIPM. The tabulated numbers are all corrections, in milligrams, to 1 kg. Least squares fitted values of the 1984 measurements have been used.

Values found at NBS in 1983

K20	1 kg − 0.019 mg (1948 BIPM certificate)
K4	1 kg − 0.090 mg
KA	1 kg − 4.891 mg
K650	1 kg − 2.292 mg

A. 1984 NBS values of K20, K4, KA, and K650 based on 1983 NBS values for KA and K650 (corrections in milligrams to 1 kilogram)

	K20	K4	KA	K650
KA	−0.045	−0.128	−4.892	−2.293
K650	−0.045	−0.127	−4.890	−2.292
Ave.	−0.045	−0.128	−4.890	−2.292
1983 value:	−0.019	−0.090	−4.891	−2.292
Δ :	−0.026	−0.038	0.001	−0.000

B. Same as A except 1983 measurement algorithm used in 1984

	K20	K4	KA	K650
KA	−0.040	−0.124	−4.891	−2.298
K650	−0.035	−0.118	−4.886	−2.292
Ave.	−0.038	−0.121	−4.888	−2.295
1983 value:	−0.029	−0.090	−4.891	−2.292
Δ :	−0.029	−0.031	0.003	−0.003

Table 9. In A, one sees that K20 and K4 give self-consistent results but the results are inconsistent with results based on CH-1 and D2. After cleaning, B shows better self-consistency and also good consistency with BIPM results. The tabulated numbers are all corrections, in milligrams, to 1 kg. Least squares fitted values of the 1984 measurements have been used.

Values found at BIPM in 1984

K20	1 kg − 0.022 mg
K4	1 kg − 0.106 mg
CH-1	1 kg − 0.384 mg
D2	1 kg + 13.447 mg

A. 1984 NBS values of K20, K4, CH-1, and D2 based on 1984 BIPM values

	K20	K4	CH-1	D2
K20	−0.022	−0.103	−0.372	13.471
K4	−0.025	−0.106	−0.376	13.467
CH-1	−0.034	−0.114	−0.384	13.459
D2	−0.046	−0.126	−0.396	13.447

B. Same as A except CH-1 and D2 cleaned prior to measurements

	K20	K4	CH-1	D2
K20	−0.022	−0.103	−0.389	13.452
K4	−0.025	−0.106	−0.392	13.448
CH-1	−0.017	−0.098	−0.384	13.456
D2	−0.027	−0.107	−0.393	13.447
Ave.	−0.023	−0.104	−0.390	13.451
BIPM values:	−0.022	−0.106	−0.384	13.447
Δ :	−0.001	−0.002	0.006	−0.004

been recalibrated using the 1981 equation of state for moist air [27]. We estimate that the calibrations of the barometer, thermometer, and humidity sensors used at the time, as well as the assumption of a background level of CO_2, introduce an additional uncertainty of about 16 μg.

Comparison of the 1970 and 1984 values suggest that D2 has lost a considerable amount of mass in the last 15 years. The loss could be due to wear because D2 has been used extensively.

A comparison of the 1984 NBS results with the 1984 BIPM calibration is shown in table 9a. Since all measurements were made at nearly the same relative humidity, no correction is necessary. There is reasonable self-consistency among K20, K4, and CH-1, but D2, appears to have gained mass. Recall, however, that we are looking at values of the stainless steel weights after they were simply dusted upon removal from their packaging. The results inferred from measurements made after the stainless steel weights were cleaned by vapor degreasing (see Appendix) are shown in table 9b. These now appear consistent with BIPM measurements (but are now less consistent with the 1983 measurements at NBS).

These results can be interpreted in so many different ways that we are forced to expand our uncertainty accordingly. Thus it appears that long-term measurements of platinum-iridium artifacts based on K20 can be stable to 10 μg provided that *the artifact is vigorously cleaned* before use, according to the BIPM method. Mass values can be supplied to stainless steel weights with an uncertainty of about 30 μg. This includes all known sources of uncertainty as well as an additional "between times" component.

We should point out, however, that other laboratories have reported somewhat better results for comparisons of platinum prototypes with stainless steel weights [41]. These results, although based on a data sample too small to be definitive, strongly suggest that the 30-μg uncertainty on stainless steel weights can be significantly reduced once the influencing effects are better understood.

Because of the difficulty of assigning an SI mass value to a stainless steel weight, it has been suggested that a practical mass system based on stainless steel or nickel-chrome artifacts be adopted. Indeed, this is essentially the approach that has been taken by NBS [42]. The danger in this approach is that the long-term stability of the artifacts is not assured to the same extent as is the stability of the national prototypes.

9. *Recommendations*

Several steps must be taken in order to improve both our ability to make reproducible mass measurements and our prospects for understanding the effects of influencing parameters:

1) Since virtually all secondary mass standards are now made of stainless steel, it is desirable for NBS to use stainless steel working standards for routine calibrations. The stability of these standards however, must be determined—not assumed. This will necessitate periodic measurements against K20 which, in turn, leads to recommendations 2) and 3).

2) A balance (preferably automated) must be made available which has a standard deviation of 1 μg or better. In all probability, the time required to complete a weighing design will always be measured in hours. This has more to do with transporting weights to the pan without creating air turbulence than with the speed of operation of the balance itself. By having a device which measures to a standard deviation of 1 μg instead of the present 4.5 μg, a single set of measurements would yield mass values with the same standard deviation as the average of 20 sets obtained using the V-1 balance. Since the mass artifacts are mutable, a balance with low standard deviation is the only practical method of acquiring necessary data with an acceptable number of weighing operations. The best mass standards seem stable enough to warrant this level of precision.

3) The balance should be enclosed in a hermetically sealed chamber. This is probably prerequisite to achieving the desired standard deviation because changes in room air pressure would otherwise lead to air currents in the balance. In any event, it is very desirable that the density of air remain constant during a complete weighing design. Such a chamber would also permit research on other possible weighing atmospheres—including reduced air densities (i.e., partial vacuum). Thus the potentially large correction for relative humidity suggested by NRLM could be verified.

4) A cleaner environment for storing and using the weights should be considered. Cleaning is a major source of instability in mass standards. Technology exists to maintain weights in environments which have greatly reduced levels of dust and hydrocarbon vapors from those of our present facility.

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Platinum-Iridium Prototypes

Since the calibration of K4 and K20 is infrequent, it is important to know as much as possible about the long-term stability of these prototypes. The question inevitably involves cleaning, because airborne pollutants inevitably increase the mass of the prototypes at an unknown rate. This rate would, presumably, be reduced if storage in a cleaner environment could be arranged. The cleaning method must return the surface of the prototype to an original condition.

After manufacture, the prototypes were cleaned with alcohol and water vapor before calibration by BIPM metrologists [6]. In the years after, prototypes returned to BIPM for calibration were wiped clean with solvent-soaked chamois skin [11]. In 1946, A. Bonhoure systematically studied various cleaning procedures and reached the following important conclusions:

- *Steam cleaning produces a more reproducible* mass than any other method.
- Steam cleaning alone is insufficient in some instances—especially when the weight surface is visibly discolored.

For these cases one must remove the dirt by rubbing with chamois skin or soft cloth soaked in a convenient solvent (benzene, alcohol, and ether were solvents actually used). This operation must be followed by steam cleaning.

- *Vigorous rubbing with chamois skin as described* above, if done with care, does not damage the weight involved.

The cleaning technique has been further perfected by Girard at BIPM who profited from the low standard deviation (~1 μg) of the NBS-2 balance for his studies. Girard used successive rubbings with chamois skins soaked in benzene and ethanol followed by steam cleaning. He showed that prototype K63 was stable to about 2 μg using such a procedure. A second platinum weight whose surface was badly scratched, however, required more than one cleaning procedure to reach a reproducible minimum mass [32].

In light of what is now known, it has been suggested that it is "not impossible" that the variability observed in measurements of prototypes between 1890 and 1946 is due to inferior methods of cleaning [43]. Indeed, it was the custom of BIPM to assume that observed changes in mass of less than 50 μg were to be expected [44].

Thus, when examining the variability of prototypes after 1890, it is reasonable to dismiss results prior to 1946. Of the remaining results, one must also exclude cases where the prototype is known to have suffered an accident. The remaining ensemble of measurements reported by BIPM has a standard deviation of 10 μg based on pooling 18 mass differences involving 13 prototypes. Data between 1891 and 1945 have been excluded.

Besides computing a pooled standard deviation, it is also interesting to see if the magnitude of the deviations has a time dependence—that is, if two calibrations of a prototype separated by several decades tend to be more discrepant than calibrations separated by a shorter period of time. We again examine only those data for weights which were steam cleaned just prior to calibration. Although the data are limited, the observed discrepancies appear flat between 10-year periods to the maximum 95-year period. The data of [32] suggest that, for periods of months, the scatter seen in repeated cleaning and calibrations is less than 2 μg. These data, however, involved a single prototype which was measured on NBS-2. Also, the period of time involved was short enough that recleaning of the reference standard was unnecessary. These two factors undoubtedly contribute to the lower scatter. In particular, from the limited data presented by Bonhoure, one can see that a significant portion of the instability of assigned mass values must have been due to the balance that was used. Now that NBS-2 has been in service for over 10 years, it will be interesting to see if the measured long-term stability of the mass values assigned to the prototypes is improved.

We might note, in addition, anomalous behavior has been observed in at least one prototype. The short-term stability of K18 (belonging to the U.K.) is rather poor [45], although the long-term stability is representative of the ensemble of prototypes. The source of the problem has not yet been discovered. This behavior indicates that one must be cautious in drawing inferences for a single prototype based on the behavior of an ensemble.

Since the U.S. has two prototypes, one would think that measurements of the mass difference between the two would provide valuable information. Such measurements are difficult to interpret, however, as can be shown by referring to table 1. The values for the mass difference of K20 and K4 presented range from 84 μg to 11 μg. This confusing picture becomes somewhat clearer upon close examination of the laboratory notebooks involved.

In particular, let us examine the data for 1947–1984. It appears that K4 was not cleaned between 1889 and 1970. In 1947, just prior to returning K20 to BIPM for recalibration, K20 was cleaned at NBS. The cleaning procedure used differed in many ways from that adopted at BIPM in 1948. It was clear from a series of measurements made at NBS that K20 actually *gained* about 20 μg as a result of the "cleaning" used. This excess, as well as additionally accumulated surface dirt was, apparently, removed in the cleaning at BIPM in 1948 so that the mass value of K20-K4 decreased by 34 μg between 1947 and 1949.

In 1970, both K20 and K4 were steam cleaned. The difference in value between 1970 and 1889 could be due to the observed surface damage on K4, noted in 1947 (see sec. 4.1).

In 1971 the kilograms were again washed with steam. The measured value for the mass of K20-K4 was low enough, however, for the metrologists involved to suspect that K4 had been insufficiently cleaned. After a vigorous recleaning, new surface damage was noticed on K4. This damage coincided with a new value of 66 μg for the mass difference.

In 1983, both K20 and K4 were cleaned several times at NBS. The procedure used was rinsing in baths of benzene and ethanol, followed by steam cleaning. The use of rinsing baths is apparently inferior to actual rubbing with solvent-soaked chamois skin. This can be seen in the BIPM data which show that the cleaning at BIPM removed an additional 21 μg from K20 and an additional 31 μg from K4.

The lesson of these data is that strict adherence to the cleaning method used by BIPM is prerequisite to obtaining both stable results and results which would obtain were the measurements conducted at BIPM.

Stainless Steel Standards

The research into the cleaning of stainless steel weights is less definitive than that concerning the prototypes. Bonhoure tried to apply the same cleaning procedure to stainless steel weights that he had found so effective for platinum-iridium. The masses of the artifacts used were measured after each step of the cleaning procedure. The final steam cleaning caused a loss in mass of about 100 μg although successive steam cleanings had no further effect [46,47]. Bonhoure also found that single-piece stainless steel weights which had been used in hydrostatic measurements might change their mass value by an appreciable amount. These changes were not permanent but recovery could take months [47]. For these reasons, it is the practice of BIPM to clean stainless steel weights exactly as platinum-iridium prototypes with the important omission of steam cleaning.

At NBS, we have used vapor degreasing in inhibited 1,1,1-trichloroethane as the final step in cleaning weights of stainless steel. Both this method and the BIPM method were used on steel spheres whose diameters were then measured optically. Dimensional measurements on the spheres which had been vapor degreased had the lower standard deviation [48]. (The exact reason for this, as well as the explanation for a systematic difference in the dimensional measurements for the two cleaning methods, is unknown.)

Vapor degreasing has proved to be an acceptable method of cleaning. A stackable set of stainless steel weights with nominal value of 1 kg was found to be stable under numerous vapor degreasing operations over a period of more than one year. The balance used had a standard deviation of 12 μg and the kilogram weight set had double the surface area of D2.

Three vapor degreasings of CH-1 did not result in any noticeable changes in mass. The measurements were carried out on the V-1 balance.

More research is required to establish both an agreed-upon method for the cleaning of stainless steel weights and an alloy with optimal qualities. Such research is being carried out under the aegis of Working Group 3 of the Consultative Committee for Mass and Related Quantities.

The long-term stability of stainless steel standards is not well established. There is no doubt that some older weights have lost mass monotonically with time [48,50]. This is probably due both to wear[1] and to outgasing. The latter component would, presumably, not be significant in vacuum melted weights. Other possible mechanisms for instabilities in stainless steel weights have recently been studied at the Istituto di Metrologia "G. Colonnetti" (IMGC) in Turin, Italy [50,51].

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[1] The hardness of annealed 90/10 platinum-iridium alloy is 130 HB. The alloy of which CH-1 is made has the same hardness. Type 18/8 stainless steel is somewhat less hard.

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A Density Comparison of Silicon Artifacts Between NML (Australia) and NBS (U.S.)

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The densities of four silicon artifacts were measured in SI units to 1×10^{-6} by NML (Australia) and NBS (U.S.). Agreement is within the experimental uncertainty of each laboratory. Two of the artifacts had been used in the determination of the Avogadro constant at NBS. The remaining two objects had been used at NBS to establish silicon density artifacts available as a Standard Reference Material (SRM).

Key words: density standards; hydrostatic weighing; international comparison; SI; silicon; volume standards.

1. Introduction

In order to compare density as measured in SI units at NML (Australia) and NBS (U.S.), four silicon transfer standards were measured in each laboratory.

The density scale at NBS is based on interferometric measurements of the diameters of four steel spheres. These measurements were terminated more than 10 years ago, but, at the time of the volume determination, density information was transferred to four single-crystal silicon objects by means of hydrostatic weighing [1].[1] NBS believes the density of these objects to be constant with time.

At NML, the volume of a hollow sphere of ultra-low expansion glass was measured interferometrically [2]. The sphere diameter was measured at various temperatures ranging from 6 °C to 40 °C, and the volume was calculated to fit a quadratic expression in temperature.

Both NBS and NML assign an uncertainty to their density or volume standards of approximately 1×10^{-6} (1 ppm) if the uncertainties are computed following BIPM recommendations [3].

In the first series of weighings, completed in 1980, two silicon crystals of approximately 100 g each were measured by NBS and NML. These crystals had been used at NBS in the determination of the Avogadro constant [4]. Their measured density at NBS and history

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[1] Figures in brackets indicate literature references.

prior to measurement by NML are given in [4], where the objects are referred to as D_1 and D_2.[2]

The second series of measurements, completed in 1983, involved comparing density measurements of two silicon crystals, each having a mass nominally equal to 200 g. The fabrication as well as the density determination of these objects at NBS are described in [5], where the objects are designated 703 and 806′. The objects were used to establish a stock of silicon artifacts of certified density. These are made available by NBS as a Standard Reference Material (SRM).

Discussion

A. First Set

The first set of measurements was undertaken informally. The motivation was simply to ascertain whether uncertainty arising from systematic behavior, which had been discovered but could not be explained [4], had been properly estimated by NBS. The unexplained behavior involved interferometric measurements of ball diameters that took on two different values depending on which of two cleaning methods had been used.

The results of the density comparison are summarized in table 1. The total uncertainty assigned by NBS is 1.0 ppm for each crystal (see table 2A). Of this 0.8 ppm is due to systematic behavior involving the cleaning of the steel balls. Thus, if this systematic behavior were understood, the NBS uncertainty could be lowered to about 0.6 ppm.

Table 1. Interlaboratory differences.

Crystal No.	Temp (°C)	Density (g/cm^3)		
		NBS	NML	Difference
D_1	20	2.3290836	2.3290824	−0.0000012 (0.52 ppm)
D_2	20	2.3290825	2.3290825	0.0000000 (0.00 ppm)

The uncertainties in the NML measurement are shown in table 2B. The uncertainty in sphere volume is a combination of the error associated with a quadratic fit to volume versus temperature (0.93 ppm), phase correction (0.3 ppm), and pressure correction (0.6 ppm).

B. Second Set

Hydrostatic measurements at NBS were carried out using techniques which have been described well elsewhere [6]. The bath temperature was nominally 23.7 °C. The thermal coefficient of expansion of the silicon reference standards was assumed to be identical to that of 703 and 806′. Therefore, no temperature correction was applied even though the results are reported at 20 °C, the temperature at which the density of the working standards is known.

No significant difference in density between 703 and 806′ could be discerned. The density of the two pieces taken together was, therefore, chosen as the datum to be compared with NML. Since the pieces are almost identical in mass and density, a simple average produces the same results as various weighting schemes which could have been used.

Data at NML were taken at three different nominal temperatures, as is shown in table 3. The measurements at 20 °C have a mean value of 2.3290708 g/cm^3 with a standard deviation of 0.43 ppm. These numbers, however, do not make use of the data taken at 4 °C and 10 °C. In order to take account of all the data available, a one-parameter fit was computed using accepted values for the thermal expansion of silicon [7]. The data of [7] were first fit to a cubic power series in the temperature region of interest. This result was then used to fit the data obtained by NML. The only adjustable parameter was the density of the silicon samples at 20 °C. Software developed at NBS proved very convenient for this analysis [8].

The result of the fit is that the density at 20 °C is found to be 2.3290719 g/cm^3 with an approximate standard deviation of 0.33 ppm. This uncertainty must be expanded to 0.37 ppm, however, to take account of the effects of the reported uncertainty in the data of [7]. The total uncertainty is the root-sum-square of 0.37 ppm and the first four items of table 2B.

Table 2A. Sources and NBS uncertainties.

Source	NBS Uncertainty [4]	
Temperature of interferometer	0.23 ppm	
Wavelength calibration	0.08	
Phase shift in reflection	0.12	
Photographic nonlinearity	0.01	
Bath temperature	0.03	
Mass of steel balls	0.18	
Mass of silicon transfer crystals	0.05	
Hydrostatic balance calibration	0.27	
Cleaning uncertainty	0.8	
Root-sum-square	0.94 ppm	
Measurements involving D_1	0.22	
Measurements involving D_2		0.44
Total Uncertainty	0.97 ppm	1.04 ppm

Table 2B. Sources and NML uncertainties.

Source	NML Uncertainty
Sphere volume measurement	1.15 ppm
Balance mass calibration	0.05
Sphere mass calibration	0.17
Silicon mass calibration	0.43
Hydrostatic weighing	0.88
Root-sum-square	1.52 ppm

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[2] Note in [4] that densities in table X are given at 20 °C but that densities in table XI are given at 25 °C.

Table 3. Mean densities in g/cm^3 of 703 and 806′ as measured at NML.

Temperature	703	806′
°C		
4	2.329 350 1	—
	2.329 349 6	2.329 349 6
10	2.329 252 4	2.329 247 0
20	2.329 072 8	2.329 074 7
	2.329 069 2	2.329 068 2
	2.329 069 3	2.329 070 8

Comparisons between the two laboratories are shown in table 4. At NBS, the mass of the two artifacts was determined by substitution weighing with a 200-g standard. The uncertainty represents the pooled standard deviation of 10 measurements. At NML, for reasons which are unclear, mass measurements of 806′ gave a slightly larger standard deviation than those of 703. Nevertheless, agreement of the mass values and density values between the two laboratories is good.

As a result of these measurements, one can infer that densities assigned to silicon artifacts are consistent with the stated uncertainties at NML and NBS.

One of us (R. S. Davis) has recently reported on similar density comparisons with the Istituto di Metrologia "G. Colonetti" (IMGC) [9]. It is interesting to note that although the discrepancies with IMGC were also within expected uncertainties, the sign of the discrepancies is the same as was found with NML.

Table 4. Summary of results.

	NBS	NML	Difference
Mass of 703:	206.57459 g	206.57465 g	60 µg (0.29 ppm)
806′:	207.76914	207.76915	10 µg (0.05 ppm)
Uncertainty : 703	50 µg (0.24 ppm)	58 µg (0.28 ppm)	
806′		89 µg (0.43 ppm)	
Density of 703 & 806′ at 20 °C:	2.3290734 g/cm^3	2.3290719 g/cm^3	−1.5µg/cm^3 (0.64 ppm)
Total Uncertainty:	2.6 µg/cm^3 (1.1 ppm)	3.0 µg/cm^3 (1.3 ppm)	

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Mass Comparator for In-Situ Calibration of Large Mass Standards

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This paper describes a high precision electronic mass comparator with a range from 250 kg to 5,000 kg. It is suggested that it would be useful to transport the comparator to the test weights rather than to transport the weights to the comparator, the usual method, thus economizing time and monies.

Key words: constant load; electronic; large weights; load cell; mass; mass comparator; portable; tolerance testing.

Introduction

In many laboratories around the world there are large dead weight testing machines used for calibrating strain gage load cells, proving rings, and other force transducers. Usually a special balance or scale for reverification of the dead-weight mass values is available should the need arise. If not, then on occasion the machine may have to be disassembled and transported to a laboratory where appropriate mass standards and weighing machines exist.

In the United States, and probably in most countries represented at the 1985 mass seminar of the International Measurement Confederation, the transportation of large mass standards, weighing many thousands of kilograms, is a daily occurrence. Usually these mass standards are in the nature of scale test weights for which the user does not need a mass value which is accurate to a few parts per million, but must only be assured that his weights are within a specified tolerance to meet the legal requirements for commerce. The tolerance placed on these test weights is approximately 1 part in 10,000. The following discussion describes a new portable electronic mass comparator. This unit can easily be transported, along with a suitable mass standard, to any site where reasonable weighing conditions exist, allowing relatively rapid and inexpensive verification of a collection of weights.

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The Mass Comparator

Although the mass comparator is described well in the literature [1,2,3,4][1] a brief description of the unit and how it operates will be useful for those not familiar with the principles.

First, as the name implies, the device is either a mass comparator or a force comparator. Since the local acceleration of gravity affects equally the mass standard and the test weight, the masses can be compared directly (assuming the displacement volumes are equal). This comparison could be made on any strain gage load cell.

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[1] Figures in brackets indicate literature references.

However, since the resulting measurement may not be accurate to within 1 part in 10,000, one could not state with assurance whether the measured test weight is in or out of tolerance.

Because a load cell has the desirable features of portability, electric signal output, small size, and the possibility of battery operation, it would be highly useful if the following disadvantages could be overcome:

1) Hysteresis
2) Creep
3) Sensitivity to off-axis loading
4) Sensitivity to torque loading
5) Unbalanced bridge self-heating
6) Sensitivity to barometric pressure variations.

The first two items on the list, hysteresis and creep, are circumvented by the most important principle of the mass comparator, which is a constant loading of the load cell at all times, even during the period when the mass standard and the test weight are being exchanged. This is accomplished with a servomechanism [1] that uses coiled springs in tension to supply the force required to automatically maintain a constant load on the cell even when the equivalent mass load is in the process of changing. Figure 1 demonstrates this principle.

The next two items on the list, sensitivity to off-axis loading and sensitivity to torque loading, can be eliminated by the placement of high-quality universal joints above and below the cell and a good-quality, robust thrust bearing at the load connecting point. These serve to keep the load axially aligned through the cell and eliminate torque that might otherwise be imparted to the cell during loading and unloading of the weights.

The last two disadvantages on the list can be avoided by fabricating a load cell and strain gage dedicated for use as a mass comparator and not as a direct-reading load cell. The bridge in an ordinary load cell is usually balanced when unloaded and goes progressively out of balance as the cell is loaded to capacity. This out-of-balance condition causes heating in the transducer and makes the measurement of very small electrical signal differences between two large signals more difficult. This out-of-balance condition can be corrected with an external bridge [4]. However, this situation lacks symmetry, and the comparator becomes very sensitive to thermal changes in the weighing environment. The best solution to the problem is to install a bridge that can be balanced for any applied load. Such a circuit is shown in figure 2. Not only is it symmetrical but lends itself to sophisticated schemes for measuring very small signal differences between applied loads.

Because the unbalance signal levels are quite small (0.01 μV) a clean, dry, bridge environment is required. However, unlike the direct-reading load cell for which long term stability (load vs. output) is desirable, it is not necessary to seal the cell with a dry gas thereby making the transducer sensitive to barometric pressure changes.

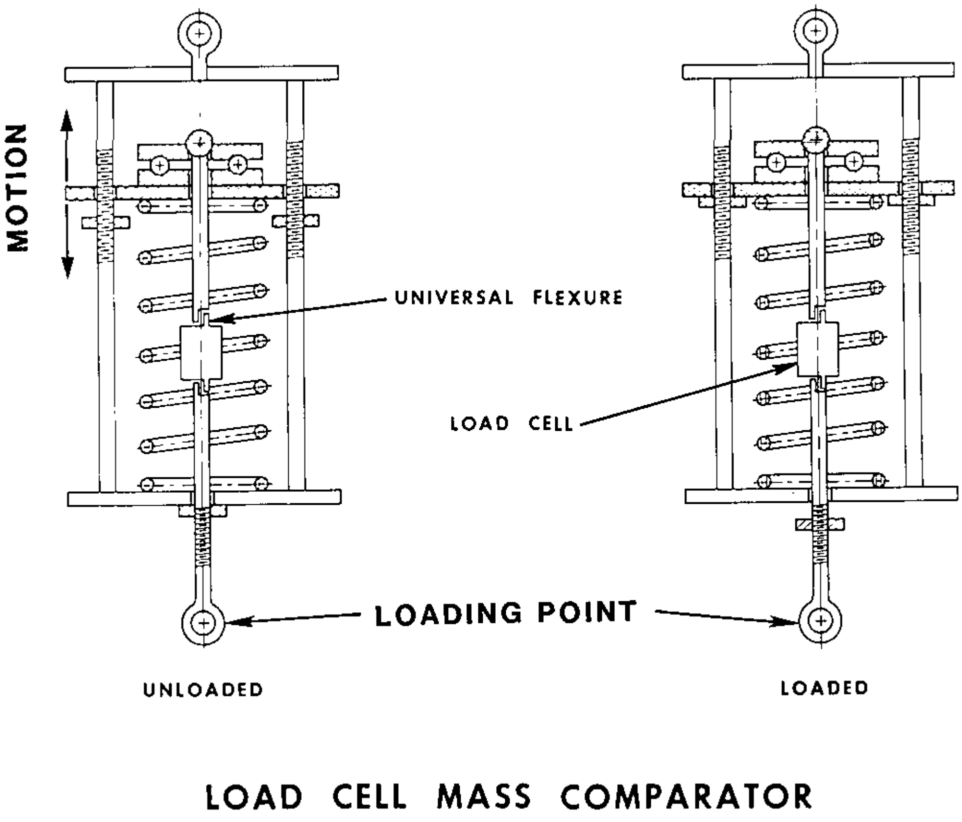

Figure 1–Servomechanism uses coiled springs in tension to supply the force required to automatically maintain a constant load on the cell.

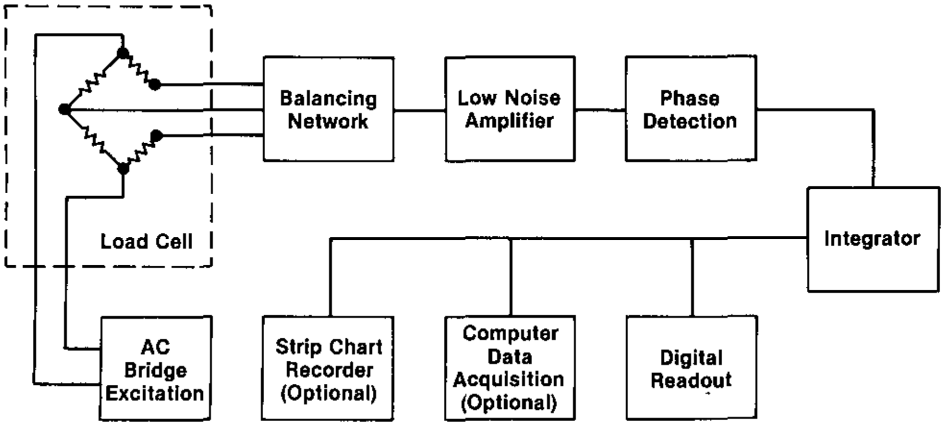

Figure 2–A symmetrical bridge that can be balanced for any applied load.

We need only keep the bridge clean and dry. When in use, the internal cavity of the load cell, depicted in figure 3, is exposed to ambient pressure via a vent and filter-dessicant package.

Although battery operation makes the comparator more versatile it is not essential. However, battery operation along with a chopper-stabilized amplifier is desirable when such small voltage levels are measured. The circuits that measure these small voltages are sensitive to power line variations and electrical noise found in many industrial facilities. Battery operation eliminates the problem and makes the instrument truly portable. However, a hybrid system is usually more desirable since the partial use of house power allows for a brighter digitial display and computer interfacing, both of which place a heavy power drain on rechargeable battery packs.

Figure 4 shows the completed mass comparator schematically. The unit has four negative springs in tension with staggered engagement to shorten the overall package length. Connected to the top of the comparator is a hydraulic cylinder for lifting the comparator a small

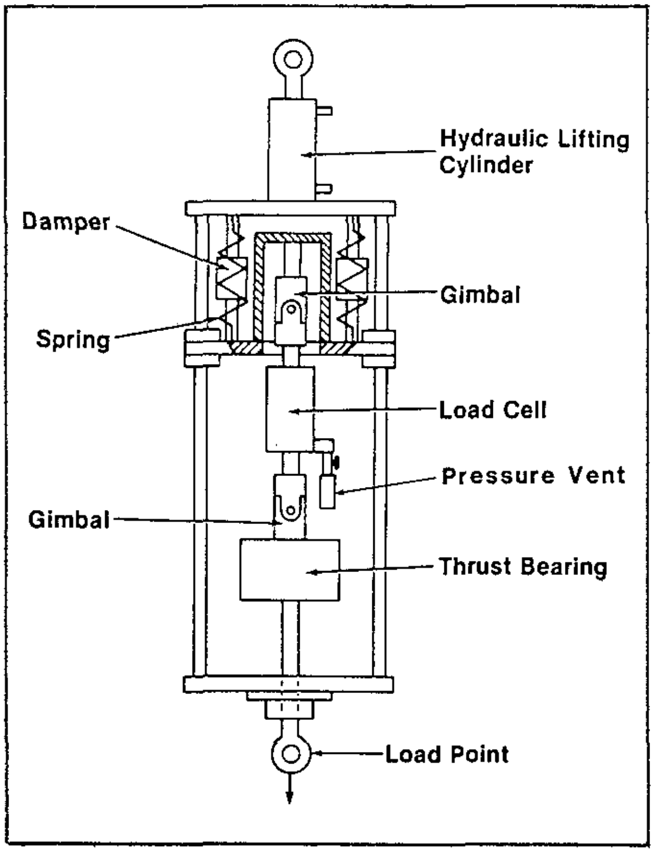

Figure 3–Internal cavity of the load cell is vented to ambient conditions.

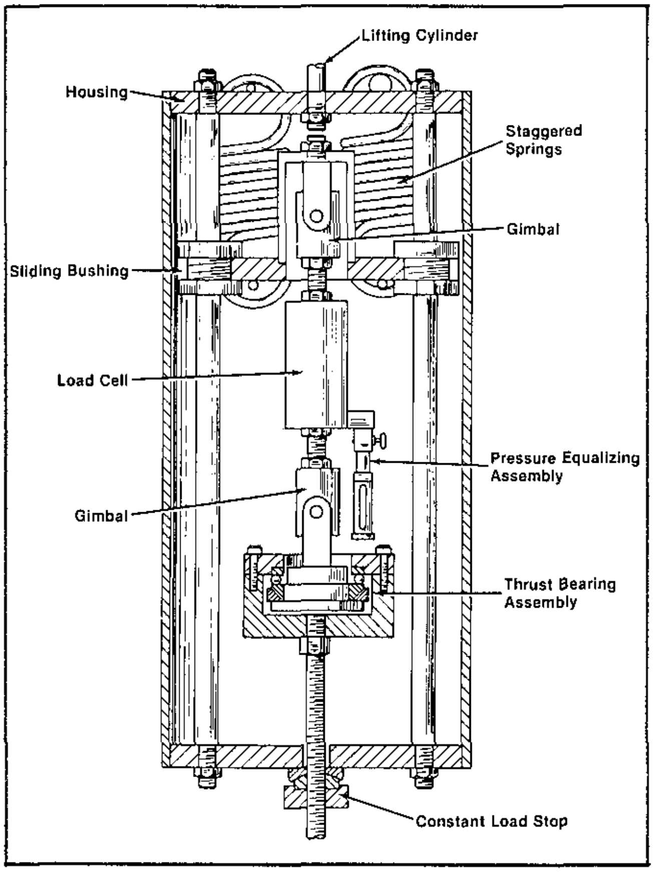

Figure 4–The completed mass comparator.

amount thereby lifting any attached test weight slowly from its resting position and gently loading the comparator. Figure 5 illustrates the principle.

In-Situ Weighing

It would seem that we would need only to carry the mass comparator and a mass standard to an area suitable for weighing to a few parts in one hundred thousand (for tolerance testing) and proceed with an appropriate comparison scheme. However, we would soon discover the need for a traveling support for the comparator such as an overhead crane or a means to move the weights beneath the comparator.

At the parts-per-million level of precision the system performs better when the comparator is suspended from a fixed point and the standard and test weight are placed directly below the load point. However, with care the performance is not badly degraded when the comparator is moved on a crane from one weight to the next. Thus we have a choice in the weight handling system to be used.

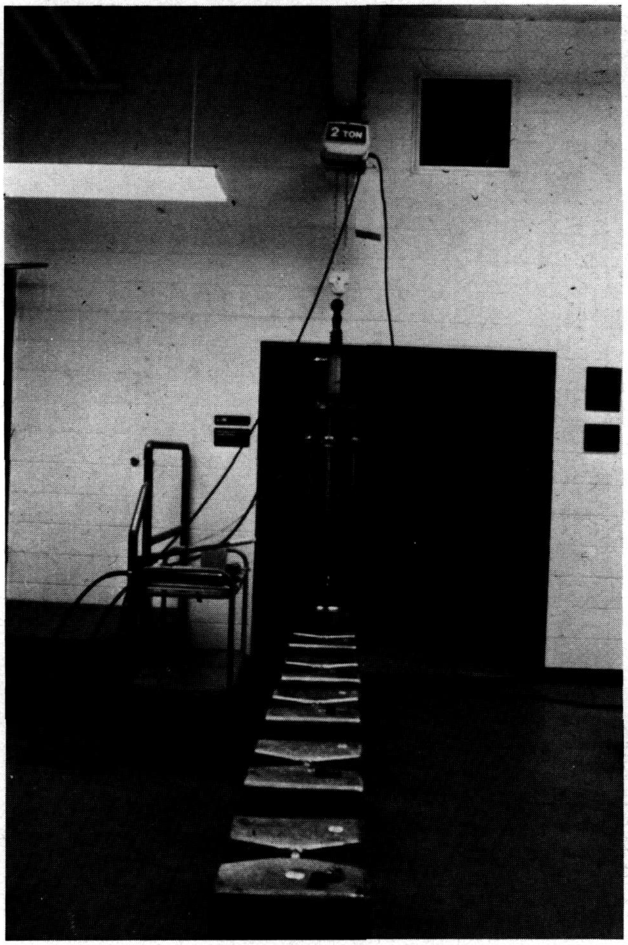

Figure 5–Hydraulic lifting for the gentle loading of the comparator.

Figure 6 shows a typical crane-mounted system for testing 500 kg test weights in the standards laboratory of the state of Illinois. The standard is picked up and the indicator is set to zero, assuming that the standard has no correction. Immediately following this, in a uniform time sequence, other weights are picked up and any differences from the mass standard are noted. After testing five weights, the operator returns the comparator to the standard and notes the indication. If a drift has occurred it is assumed to have been linear with time and the test weight observations are then corrected based on a uniform time sequence as follows:

$$O'_{xi} = O_{xi} + \frac{(O_N - O_1)(t_{xi} - t_1)}{t_N - t_1}$$

where O_1 and O_N are respectively the first and last observations of the standard, and t_1 and t_N are the corresponding times. O_{xi} and t_{xi} are respectively the observed mass difference and the time for each test weighing, and O'_{xi} is the difference corrected for drift.

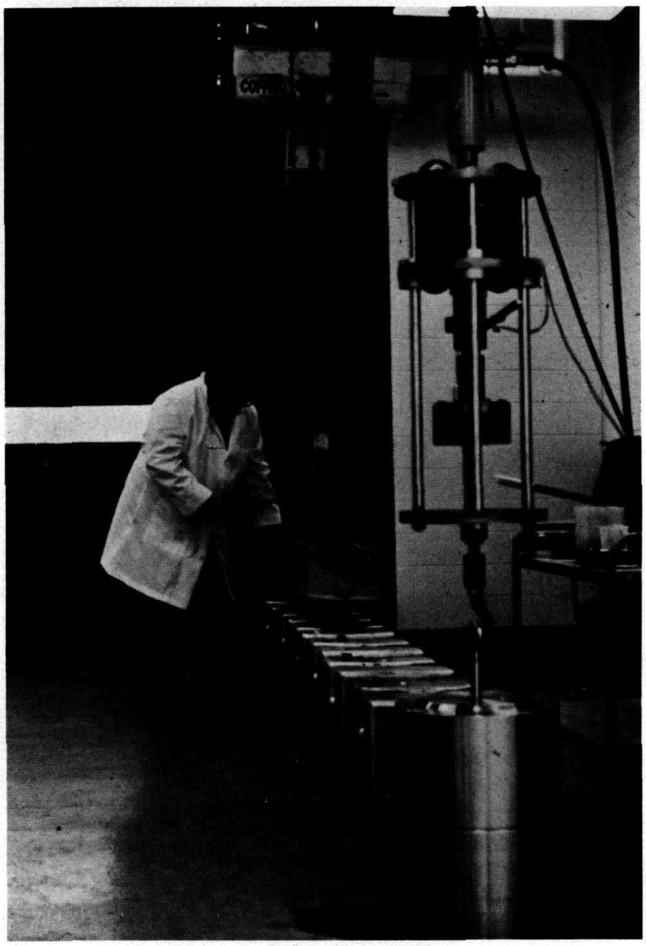

Figure 6–Crane-mounted system for testing 500 kg test weights in the Illinois standards laboratory.

Using the scheme of figure 6 or any suitable method we could mount the comparator at a fixed position and move the standard and test weights to the comparator. This method works well with a track-and-dolly system shown schematically in figure 7 for weights of 1000 kg or less. When larger loads are encountered, especially near the capacity of the comparator (5000 kg), an air supported cart such as shown in figure 8 is very useful. Here all that is required besides the cart and its power unit is a flat, smooth concrete floor and some temporary guide rails.

It should be noted that there are many algorithms in use to establish whether or not mass values are in tolerance. The algorithm discussed here is only one example of how the substitution weighing could be performed. The method chosen is largely dependent on the comparator's zero stability and the weighing environment. Some weighing environments undergo large and rapid temperature excursions. For those conditions, the above example would not be the one of choice. It may be possible to weigh outdoors with this device if adequate protection from the sun and wind are provided. When more than a simple tolerance test is desired, as in a mass value assignment, then more elaborate comparison methods may be required along with more stringent environmental controls.

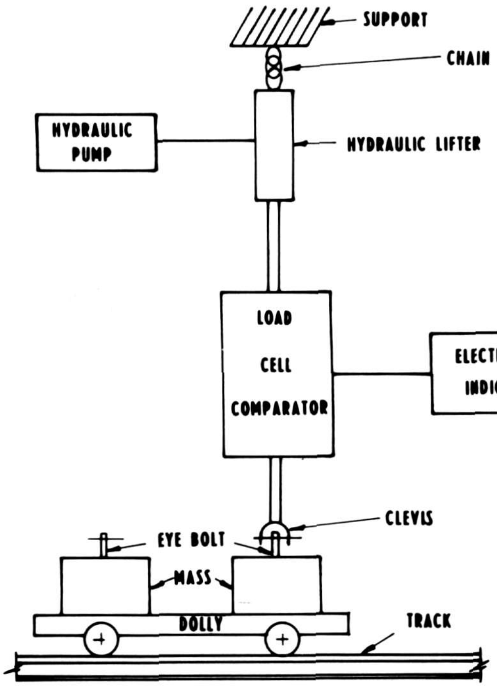

Figure 7–Track-and-dolly system for moving the standard and test weights to the comparator (for weights of 1000 kg or less).

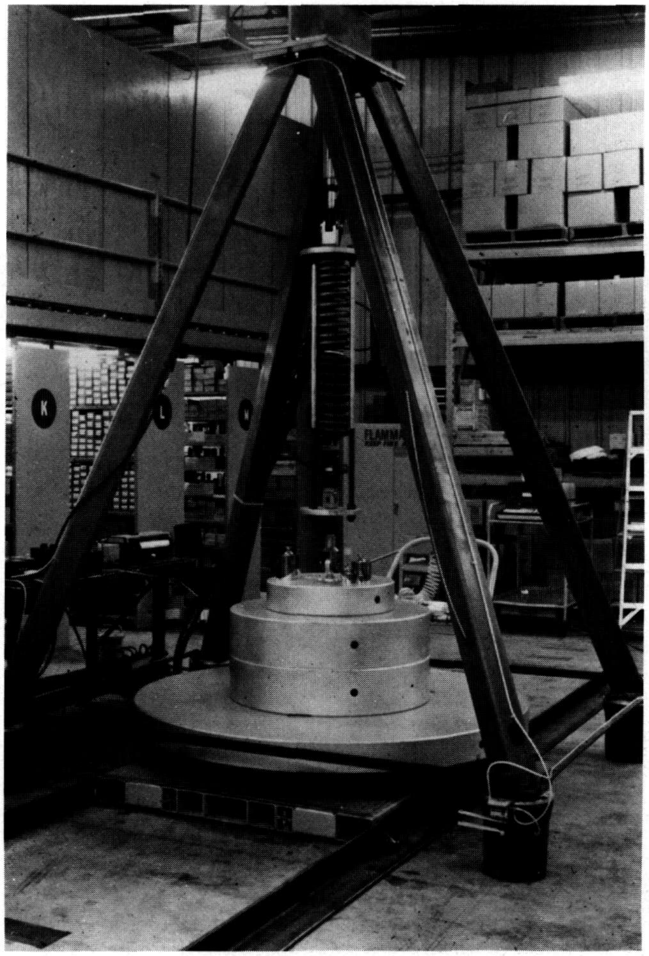

Figure 8–Air supported cart is useful for large loads.

Other Applications

The figures have demonstrated the portability and in-situ weighing capability of the load cell mass comparator. Figure 9 demonstrates the usefulness when weighing a mass of extraordinary geometry. The 500 kg cart shown here is undergoing a calibration that cannot be performed on most large equal arm balances because of its shape. Similar situations occur when weighing uranium hexafluoride shippping containers or during weighings used in some volumetric determinations.

Two features of the load cell not yet treated are its constant sensitivity and linearity over a restricted portion of its capacity. These features can be combined to build a comparator with part-per-million reproducibility and a capacity of from 250 kg to 5000 kg, and which can tolerate differences as large as ±1 kg between the mass standard and the test weight. By changing a switch in the electronic circuit, the comparator changes reproducibility from 1 to about 20 parts per

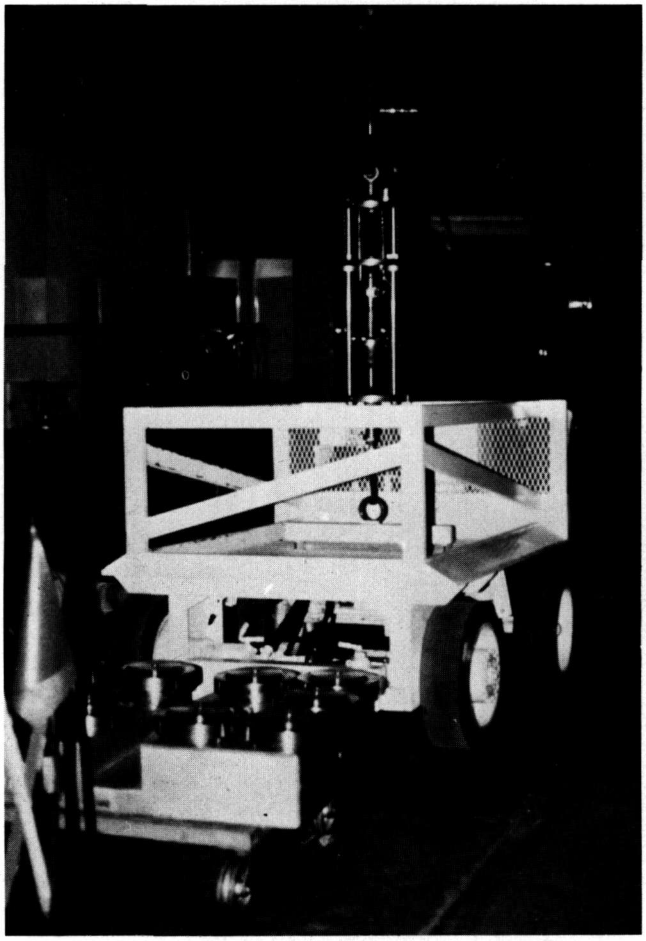

Figure 9–The load cell mass comparator can weigh a mass of extraordinary geometry, as it is shown weighing a 500 kg cart.

million and likewise can tolerate differences of ±10 kg between two weights. A third switch position allows for this progression to occur a third time. This feature makes the comparator extremely useful when test weights are reconditioned. For reconditioning, the adjustment cavities are first opened. The mass is then trimmed into tolerance by adding or removing material and then resealing the cavity. During this procedure the large "on scale" range and fast response time will often permit the mass readjustment and tolerance testing to occur simultaneously.

Conclusion

Development of the load cell mass comparator has made it possible to transport a highly reproducible mass comparator to large collections of weights that require calibration. Although several of the commercial units as well as several private units are in operation, no one has used it to perform in-situ measurements. Recent communication with the principal metrologist for the State of California indicates that California will soon undertake this program on a routine-service basis. Clearly the California program and its outcome will be of great interest to those of us engaged in mass calibration.

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Determination of the Enthalpies of Combustion and Formation of Substituted Triazines in an Adiabatic Rotating Bomb Calorimeter

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To obtain reliable thermodynamic data on substituted triazines, *it is necessary to use a calorimeter that* is capable of high precision with small quantities of sample and in which a homogeneous solution of the corrosive combustion products can be maintained. The enthalpies of combustion of six substituted triazines have been determined in a platinum-lined adiabatic rotating bomb calorimeter. These are the first determinations of enthalpies of combustion or formation to have been reported for these compounds. The values *derived for the enthalpies of formation in kJ/mol* at 25 °C are as follows: 2,4,6-trimethoxy-1,3,5-triazine, −478.60±0.87; 2,4,6-triethoxy-1,3,5-triazine, −584.99±1.50; 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −1109.80±1.53; 2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −697.08±1.15; 2-methoxy- 4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −907.71±2.40; 2-amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −773.12±1.50.

Key words: adiabatic calorimeter; aneroid calorimeter; combustion; enthalpy; fluorine compounds; formation; heat; rotating bomb calorimeter; thermochemistry; triazines.

1. Introduction

The triazines comprise an interesting group of compounds for which few data on the enthalpies of combustion and formation exist in the available literature. This is probably due to the difficulty of preparation and purification of these materials.

The parent compound, symmetrical triazine (s—$C_3H_3N_3$), which is unstable in the presence of moisture,has been studied previously. Preliminary values for the enthalpy of combustion were reported by Berets [1][1] who obtained −424.8±0.5 and 12.2 kcal/mol[2] for the enthalpies of combustion and vaporization, respectively, at 25 °C. A more recent determination by K. Arvidsson of the University of Lund, Sweden [2] yielded values of −426.06±0.22 and 13.20±0.03 kcal/mol and K. Bystrom, also of the University of Lund [3] obtained values of −425.66 and 12.95±0.05 kcal/mol, respectively, for these quantities.

Some calorimetric measurements on substituted triazine derivatives have been carried out. For example, Berets [1], Lemoult [4] and Selivanov et al. [5] determined the heat of combustion of cyanuric acid, $C_3N_3(OH)_3$, at 25 °C. Melamine, 2,4,6-

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[1] Figures in brackets indicate literature references.

[2] 1 thermochemical calorie= 4.184 joules.

amino-1,3,5-triazine, ($C_3N_3(NH_2)_3$), has also been studied by Tauernier and Lameroux [6], Salley and Gray [7], and Lemoult [8], respectively. Other related compounds for which calorimetric determinations of thermochemical properties have been reported are 1,3,5-triphenyl-1,3,5-triazine-2,4,6-trione [9], 2,4,6-triphenoxy-1,3,5-triazine [9], 2,4,6-trichloro-1,3,5-triazine [10], 6-amino-1,3,5-triazine [9], 4,6-diamino-1,3,5-triazine-2-one [9], hexahydro-1,3,5-trinitroso-1,3,5-triazine [11,12], 1,3,5-trinitro-1,3,5-triazine [11,12], 2,4-dichloro-6-ethylamine-1,3,5-triazine [13], 2-chloro-4,6-bis(ethylamine)-1,3,5-triazine [13], 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine [13], and 2-chloro-4,6-bis(isopropyl-amino)-1,3,5-tri-azine [13].

This investigation reports the values for the enthalpies of formation of symmetrical triazines substituted with fluorine, nitro and alkyl or alkoxy groups, determined using an adiabatic rotating bomb calorimeter. These substituted derivatives of symmetrical triazine present certain problems for calorimetric measurements. First, they are difficult to prepare and to purify except in very small quantities, which means that the calorimeter used in the measurements must be capable of making high precision measurements on very small quantities of sample. Second, the combustion products of the compounds studied in this investigation are carbon dioxide, nitrogen, water, hydrofluoric acid, and nitric acid. Therefore, in order to obtain reliable calorimetric data for these compounds, the bomb must be rotated to obtain a homogeneous solution of the aqueous acids, and the interior of the bomb must be lined with platinum to prevent corrosion.

2. Materials

The triazine samples were obtained from Picatinny Arsenal through the courtesy of V. I. Siele. All were colorless crystalline materials, had very low vapor pressure, were nonhygroscopic and stable in moist air. Because of the rather long chemical names, the materials have been designated as Triazine I, Triazine II, etc., in the sections of this paper that follow:

- 2,4,6-Trimethoxy-1,3,5-triazine **Triazine I**

The Picatinny label was: 762-50-77, mp 135–137 °C. No further purification was attempted.

- 2,4,6-Triethoxy-1,3,5-triazine **Triazine II**

The Picatinny label was: 762-50-78, bp 101 °C at 0.6 mm. The melting point was found to be 27.5 °C. No purification was attempted.

- 2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine III**

The Picatinny label was: 51-55, mp 76–77 °C. An attempt was made to further purify a portion of this material by a zone-melting technnique; however, no difference was observed in the energy of combustion or in the stoichiometry of the combustion products between the treated and untreated portions.

- 2,4-Dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine IV**

The Picatinny label was: 762-50-59-1, mp 54–56 °C. No purification was attempted.

- 2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine V**

The Picatinny label was: 51-54, mp 98.5–100 °C. No purification was attempted.

- 2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine VI**

The Picatinny label was: 762-50-57-1, mp 91–92.5 °C. No purification was attempted.

Benzoic Acid—The benzoic acid used for the calibration experiments was Standard Reference Material 39i, obtained from the National Bureau of Standards' Office of Standard Reference Materials. The purity was given as 99.997 mol%.

Oxygen—Commercial oxygen was purified by passing successively through an oxidizer containing copper oxide at 450 °C, a carbon dioxide absorber, and a drier containing magnesium perchlorate. In some experiments a cylinder of high purity oxygen was used; analysis showed the following maximum concentrations of impurities in ppm: N_2, 3.0; H_2O, 2.0; and N_2O, 0.8. The presence of these impurities in the given concentrations would not significantly affect the results of this investigation. There was no apparent difference between the results obtained using the two samples of oxygen.

3. Calorimetric Apparatus

An adiabatic rotating bomb calorimeter, designed and constructed by the present authors at this laboratory and described in ref. [14], was used for all measurements in this investigation. The bomb is completely lined with platinum to prevent reaction with corrosive solutions, and can be rotated to insure a homogeneous solution of the bomb liquid. The adiabatic feature results in a low heat capacity, approximately 2500 J/K, to permit high precision with relatively small quantities of sample. The bomb is surrounded by an adiabatic shield, automatically maintained at the temperature of the bomb; the calorimeter is enclosed within a jacket and is operated under high vacuum. The volume of the bomb is 98 cm^3.

Temperatures are determined by means of a capsule-type platinum resistance-thermometer located within the bomb wall. A heater, also located within the bomb wall, serves to preheat the bomb to the desired initial temperature. The thermometer is connected in series with a 27.5 Ω standard resistor, a variable resistor and a 2 V storage cell. The standard resistor is enclosed in a thermostat which is controlled at 30.6 °C. The thermometer current is 5 mA. The potential leads of the resistor are connected to the standard cell terminals of an L&N microvolt potentiometer which had been altered to tap off 1.000 V instead of 1.018 V. The potential leads of the thermometer are connected to the emf terminals of the potentiometer. The working current of the potentiometer was adjusted such that the potential reading across the 27.5 Ω resistor was 1.000 with a current of 5 mA. The actual voltage corresponding to a dial reading of 1.0000 is, therefore, 0.1375 V. The emf reading is, therefore, the ratio of the resistance of the thermometer to that of the standard resistor. A nanovoltmeter used as a detector permits the measurement of temperature within $\pm 15 \times 10^{-6}$ °C.

Ignition of the sample is accomplished by discharging an 18,000 μF condenser, previously charged to about 23 V, through a platinum wire fuse in contact with the sample. From the drop in potential across the condenser, the quantity of electrical energy can be calculated. By means of separate experiments it was found that 67% of the calculated energy was actually dissipated within the calorimeter; this factor was used to determine the actual quantity of ignition energy.

Since this is a dry (aneroid) bomb (not surrounded by water), the rotation which is carried out to produce uniform product concentrations inside the bomb does not produce enough energy to require any corrections to be made for this rotation.

4. Procedure

The approximate quantity of sample required was pressed into a pellet and weighed in a small platinum crucible using a microbalance. All weights were corrected to weights in vacuum by means of buoyancy corrections derived from the density of the sample and air-density measurements at the time of weighing. The crucible was supported in the bomb so that the sample was in contact with a 2 cm length of 0.075 mm diameter platinum wire connected between the bomb electrodes. The quantity of water initially placed in the bomb was 0.3 cm^3 for the benzoic acid calibration experiments and for those materials which did not contain fluorine; 3.00 cm^3 of water was used for the fluorine-containing compounds.

The bomb was then closed, flushed with 1 liter of oxygen and filled to 3.204 MPa (31.62 atm) with purified oxygen. The bomb was placed in the calorimeter, the filling temperature was observed and the calorimeter jacket was evacuated. The adiabatic temperature controls were placed in operation and the calorimeter was heated to approximately 24.98 °C. The calorimeter was left overnight with the vacuum pumps and the temperature controls in operation. While this period of time was much longer than required for thermal equilibrium to be established, the experiments were performed in this manner so that the calorimetric experiment, the analyses of the combustion products, and the preparation for the next experiment could be completed during the working day.

On the following morning the calorimeter temperatures were observed at intervals of a few minutes during a 45 min initial rating period. The sample was then ignited and rotation of the bomb was initiated approximately 2 min after firing. After about 20 min, thermal equilibrium was approached and temperatures were observed at intervals of a few minutes during a final rating period. Rotation of the bomb was omitted for the benzoic acid calibration experiments. Because of the heating effect of the 5 mA current through the platinum resistance thermometer, there was a constant rise in temperature of approximately 1 K/h. The initial and final calorimeter temperatures were obtained by extrapolation of the initial and final time-vs-temperature curves to the actual time of ignition.

The bomb was removed from the calorimeter and the gaseous contents released slowly through a weighed carbon dioxide absorption tube [15]; a stream of CO_2-free air was passed through the bomb at 100 cm^3/min for approximately 1 h to complete transfer of carbon dioxide. The absorption tube was flushed with dry hydrogen before weighing to reduce the effect of displacement of oxygen by the sodium carbonate formed.

The bomb was opened and the liquid contents transferred to a weighed polyethylene bottle taking care that the liquid made no contact with anything other than platinum and polyethylene. The bottle, together with the solution and washings, was weighed. A weighed aliquot was placed in a polyethylene titration flask which contained a plastic-coated stirring bar. A stream of CO_2-free air was passed through the stirred solution for 1 h to remove the dissolved carbon dioxide. Slightly less than the theoretical quantity of standard alkali was added from a buret, a combination calomel-glass electrode was introduced, and the titration was completed using a pH meter.

A second aliquot was taken for the determination of nitric acid by a micro-Kjeldahl procedure in which the acid was converted to ammonia and collected in an excess of standard sulfuric acid. Back titration with standard alkali gave the quantity of nitric acid in the aliquot. The quantity of hydrofluoric acid should be given by the difference between the total acidity and the acidity of the nitric acid, determined as described above, if no other acids are present. In order to verify the quantity of hydrofluoric acid, a few of the aliquots were titrated using a fluoride selective electrode. The results obtained by repetitions of the Kjeldahl procedure for nitric acid determination varied by as much as 10%, probably because the acid concentrations were very low. The quantity of nitric acid was, therefore, taken as the difference between the total acidity and the theoretical quantity of hydrofluoric acid.

5. Results and Discussion

The certified calorific value for the benzoic acid used for calibration of the calorimeter was 26434±3 J/g under certificate conditions. This reduces to $\Delta U\,^\circ C = -26412.35 \pm 3.0$ at 26 °C and -26410.36 ± 3.0 at 28 °C for the change in internal energy under standard conditions.

The densities of the materials, when not given with the other sample data, were determined by an approximate flotation procedure. Values for the heat capacity were estimated. The compressibility coefficients for the triazines were taken as 0. The values used in the calculations are given in table 1.

All calculations are based upon the 1971 Table of Atomic Weights [16].

All computations of Washburn corrections were by computer using a program originally prepared by C. H. Shomate of the Naval Ordinance Test Station, China Lake, CA, and modified to include compounds containing fluorine by G. T. Armstrong and E. J. Prosen of the National Bureau of Standards according to the method of Hubbard, Scott, and Waddington [17].

The results of the CO_2 analyses are given in table 2.

The results of the benzoic acid calibration experiments are given in tables 3, 4, and 5. The terms used in the tables are described as follows:

EEE-std, the effective energy equivalent of the standard, empty calorimeter at the standard mean temperatue of the experiment;

Table 1. Values taken for density, heat capacity, and compressibility coefficient.

	Density $g{\cdot}cm^{-3}$	Cp $J{\cdot}g^{-1}{\cdot}K^{-1}$	$\left(\frac{\partial V}{\delta P}\right)$ $cm^3{\cdot}g^{-1}{\cdot}K^{-1}$
Benzoic acid	1.320	1.21	4.4×10^{-4}
Triazine I	1.316	2.32	0
Triazine II	1.150	2.26	0
Triazine III	1.795	1.17	0
Triazine IV	1.700	1.64	0
Triazine V	1.720	1.31	0
Triazine IV	1.771	1.17	0

Table 2. Results of the carbon dioxide analyses.

	No. of Expts.	$CO_{2(found)}/CO_{2(theor.)}$
Triazine I	5	0.9982±0.0009
Triazine II	5	.9979±0.0008
Triazine III	7	1.0028±0.0004
Triazine IV	6	0.9999±0.0002
Triazine V	5	1.0005±0.0004
Triazine VI	6	1.0000±0.0004

Table 3. Results of the benzoic acid calibration experiments for Triazine I.

Expt. No.	**91**	**92**	**93**	**104**	**107**	**110**
EEE-Std, $J{\cdot}K^{-1}$	2512.90	2513.28	2513.28	2513.25	2513.32	2513.20
Cv-cont (i), $J{\cdot}K^{-1}$	4.79	4.79	4.77	4.88	4.87	4.88
Corr to tm, $J{\cdot}K^{-1}$	0.12	0.16	0.12	0.18	0.06	0.12
Corr-parts, $J{\cdot}K^{-1}$	0.00	0.00	0.00	−0.36	−0.36	−0.36
EEE-actual, $J{\cdot}K^{-1}$	2517.81	2518.22	2518.27	2517.95	2517.89	2517.84
Temp rise, K	3.150904	3.164264	3.167566	3.206961	3.086207	3.170323
Q-total, J	−7933.37	−7968.32	−7976.78	−8704.95	−7770.73	−7982.35
q-ign, J	1.02	1.05	0.90	1.06	1.19	1.16
q-decomp HNO_3, J	0.33	1.62	0.45	0.45	0.63	0.82
q-WC, J	6.13	6.16	6.13	6.39	6.14	6.32
q-corr to 28 °C, J	−0.05	−0.06	−0.05	−0.07	−0.03	−0.05
Q-std react, J	−7925.93	−7959.55	−7969.35	−8067.12	−7762.80	−7974.11
M_s, g	.300107	.301380	.301751	.305453	.293930	.301931
$\Delta U\,^\circ C$ (28 °C), $J{\cdot}g^{-1}$	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36
Mean EEE-std, $J{\cdot}K^{-1}$	2513.22					
sdm	±.12					

Table 4. Results of the benzoic acid calibration experiments for Triazine II.

Expt. No.	253	255	265	281	282	283
EEE-Std, J·K^{-1}	2514.17	2514.10	2514.08	2514.48	2514.26	2514.04
Cv-cont (i), J·K^{-1}	4.56	4.56	4.58	4.45	4.44	4.59
Corr to tm, J·K^{-1}	.07	.08	.10	.09	.09	.13
Corr-parts, J·K^{-1}	0.00	0.00	0.00	.00	.00	.00
EEE-actual, J·K^{-1}	2518.81	2518.74	2518.76	2519.02	2518.79	2517.76
Temp rise, K	1.077327	1.084430	1.103032	1.088817	1.075373	1.146946
Q-total, J	−2713.58	−2731.39	−2778.27	−2742.75	−2708.63	−2888.88
q-ign, J	.97	.97	.88	.83	1.01	.90
q-decomp HNO$_3$, J	.31	.08	.07	.22	.02	.15
q-WC, J	1.95	1.96	2.01	1.98	1.95	2.10
q-corr to 26 °C, J	−.01	−.01	−.01	−.02	−.02	−.02
Q-std react, J	−2710.39	−2728.39	−2775.32	−2739.75	−2705.67	−2885.75
M$_s$, g	.102618	.103300	.105077	.103730	.102440	.109257
ΔU°C (26 °C), J·g^{-1}	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35
Mean EEE-std, J·K^{-1}	2514.19					
sdm	±.07					

Table 5. Results of the benzoic acid calibration experiments for Triazine III, IV, V, and VI.

Expt. No.	160	162	165	172	184	188	200
EEE-Std, J·K^{-1}	2514.80	2514.78	2514.72	2515.05	2514.85	2514.75	2515.00
Cv-cont (i), J·K^{-1}	4.48	4.48	4.48	4.48	4.60	4.57	4.57
Corr to tm, J·K^{-1}	.10	.06	.07	.10	.28	.12	.07
Corr-parts, J·K^{-1}	0.00	0.00	0.00	.00	.00	.00	.00
EEE-actual, J·K^{-1}	2519.38	2519.32	2519.27	2519.63	2519.73	2519.45	2519.64
Temp rise, K	1.046650	1.060647	1.071820	1.084813	1.325942	1.117483	1.068379
Q-total, J	−2636.91	−2672.11	−2700.20	−2733.33	−3341.02	−2815.44	−2691.93
q-ign, J	.97	.94	1.02	.85	.98	.86	.90
q-decomp HNO$_3$, J	.24	.24	.31	.33	.31	.25	.27
q-WC, J	1.85	1.87	1.90	1.92	2.45	2.04	1.94
q-corr to 26 °C, J	−.01	−.01	−.01	−.01	−.05	−.02	−.01
Q-std react, J	−2633.86	−2669.05	−2696.99	−2730.23	−3337.33	−2812.31	−2688.83
M$_s$, g	.099721	.101053	.102111	.103369	.126355	.106477	.101802
ΔU°C (26 °C), J·g^{-1}	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35
Mean EEE-std, J·K^{-1}	−2514.85						
sdm	±.05						

Cv-cont(i), the heat capacity of the initial bomb contents including the crucible, sample, water, and oxygen;

Corr to t$_m$, a correction to the heat capacity of the calorimeter for deviation of the actual mean temperature of the experiment from the standard mean temperature;

Corr-parts, a correction to the heat capacity of the calorimeter for alterations during the series of experiments;

EEE-actual, the effective energy equivalent of the actual initial calorimeter system at the actual mean temperature of the experiment;

Temp. rise, the observed increase in temperature of the calorimeter following combustion of the sample;

Q-total, the total quantity of energy evolved by the overall bomb process, obtained as the product of EEE-actual and the temperature rise;

q-ign, the electrical energy added to the calorimeter system to ignite the sample;

q-decomp HNO$_3$, the calculated quantity of energy required to decompose any nitric acid, formed in the combustion process, into nitrogen (g) and water (liq) using 59.7 kJ/mol;

q-WC, the Washburn correction [17,18] applied to convert reactants and products to their respective standard states at the actual final temperature;

q-corr to std t_f, a correction applied for deviation of the actual final temperature from the selected standard final temperature;

Q-std react, the energy evolved by the reaction with reactants and products in their respective standard states at the selected final temperature, obtained as the algebraic sum of Q-total and the energy corrections;

m_s, the mass of sample;

ΔU°C, the energy evolved by the standard reaction at the selected final temperature for the constant volume process.

The values in the tables were taken from the computer printout and have been rounded for convenience. For this reason, slight differences from the more exact computer results may result by calculation from the tabulated values. For the calibration experiments the value for EEE-std was obtained from ΔU °C using an iterative procedure. Three separate series of calibration experiments were performed because of significant changes in the calorimeter system and in the selected temperature increment.

The results of the combustion experiments on the triazines are given in tables 6, 7, 8, 9, 10, and 11.

The values given in the tables correspond to the following reactions:

(1) 2,4,6-Trimethoxy-1,3,5-triazine **Triazine I**
$C_6H_9O_3N_3(c) + 6.75\ O_2(g) \rightarrow 6\ CO_2(g) + 1.5\ N_2(g) + 4.5\ H_2O(liq)$
$\Delta U\ °C(28\ °C) = -18524.3 \pm 4.9$ J/g.

Table 6. Results of the Triazine I combustion experiments.

Expt. No.	99	100	101	102	103
EEE-Std, $J \cdot K^{-1}$	2513.22	2513.22	2513.22	2513.22	2513.22
Cv-cont (i), $J \cdot K^{-1}$	5.38	5.37	5.41	5.38	5.38
Corr to tm, $J \cdot K^{-1}$	.07	.08	.14	.08	.07
Corr-parts, $J \cdot K^{-1}$	.00	.00	.00	−.01	−.36
EEE-actual, $J \cdot K^{-1}$	2518.67	2518.67	2518.71	2518.66	2518.31
Temp rise, K	3.096776	3.112201	3.175631	3.102691	3.101981
Q-total, J	−7999.76	−7838.61	−7998.68	−7814.64	−7811.74
q-ign, J	.98	.95	1.56	1.08	1.08
q-decomp HNO_3, J	37.09	37.02	38.41	37.02	36.87
q-WC, J	6.22	6.22	6.39	6.23	6.22
q-corr to 28 °C, J	.00	.00	.00	.00	.00
Q-std react, J	−7755.47	−7794.41	−7952.31	−7770.31	−7767.57
m_s, g	.418671	.420776	.429295	.419443	.419321
ΔU °C (28 °C), $J \cdot g^{-1}$	−18524.01	−18523.91	−18524.12	−18525.32	−18525.14
Mean, ΔU ° (28 °C), $J \cdot g^{-1}$	−18524.30				
sdm	±0.26				

Table 7. Results of the Triazine II combustion experiments.

Expt. No.	267	268	269	270	274	272[a]
EEE-Std, $J \cdot K^{-1}$	2514.19	2514.19	2514.19	2514.19	2514.19	2514.19
Cv-cont (i), $J \cdot K^{-1}$	4.78	4.72	4.70	4.71	4.69	4.68
Corr to tm, $J \cdot K^{-1}$	.36	.10	.07	.09	.11	7.16
Corr-parts, $J \cdot K^{-1}$	.00	.00	.00	.00	.00	.00
EEE-actual, $J \cdot K^{-1}$	2519.33	2519.00	2518.96	2518.99	2518.98	2526.03
Temp rise, K	1.394706	1.101912	1.063056	1.092145	1.108613	1.087068
Q-total, J	−3513.73	−2775.72	−2677.80	−2751.10	−2792.58	−2745.96
q-ign, J	.95	.88	.83	.97	.90	.83
q-decomp HNO_3, J	11.53	8.65	8.70	9.41	9.72	8.45
q-WC, J	2.06	1.61	1.54	1.58	1.60	1.57
q-corr to 26 °C, J	−.03	−.01	−.00	−.01	−.01	−.26
Q-std react, J	−3499.21	−2764.59	−2666.73	−2739.14	−2780.37	−2735.36
M_s, g	.146350	.115652	.111537	.114566	.116265	.114194
ΔU°C (26 °C), $J \cdot g^{-1}$	−23909.87	−23904.35	−23908.94	−23908.89	−23914.14	−23953.74
Mean E E-std, $J \cdot K^{-1}$	−23909.24					
sdm	±1.56					

[a] Burned as liquid at 30 °C, not included in average.

Table 8. Results of the Triazine III combustion experiments.

Expt. No.	182	185	186	276	278	279
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), J·K^{-1}	16.01	16.01	16.02	16.01	15.98	15.99
Corr to tm, J·K^{-1}	−0.01	0.00	0.01	0.00	−0.01	−0.01
Corr-parts, J·K^{-1}	.00	.00	.00	−0.70	−0.70	−0.70
EEE-actual, J·K^{-1}	2530.85	2530.87	2530.87	2530.16	2530.12	2530.13
Temp rise, K	.989164	.981087	.982180	1.009298	.980954	.963102
Q-total, J	−2503.43	−2483.00	−2485.77	−2553.69	−2481.93	−2436.77
q-ign, J	1.02	.88	.99	.90	.99	.94
q-decomp HNO_3, J	16.04	15.22	15.44	14.95	15.16	17.45
q-WC, J	6.92	6.89	6.89	7.10	6.88	6.74
q-corr to 26 °C, J	0.00	0.00	0.00	0.00	0.00	0.00
Q-std react, J	−2749.45	−2460.01	−2461.45	−2530.73	−2458.90	−2411.66
M_s, g	.345488	.342742	.343138	.352485	.342530	.336088
ΔU°C (26 °C), J·g^{-1}	−7176.65	−7177.43	−7176.28	−7179.68	−7178.66	−7175.67
Mean EEE-std, J·K^{-1}	−7177.40					
sdm	±.62					

Table 9. Results of the Triazine IV combustion experiments.

Expt. No.	190	191	192	193	194
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), J·K^{-1}	15.99	15.96	15.97	15.97	15.96
Corr to tm, J·K^{-1}	.11	−.12	.07	.06	.05
Corr-parts, J·K^{-1}	.00	.00	.00	.00	.00
EEE-actual, J·K^{-1}	2530.95	2530.69	2530.89	2530.87	2530.86
Temp rise, K	1.108844	1.043991	1.085806	1.063969	1.043179
Q-total, J	−2806.43	−2642.02	−2748.06	−2692.77	−2640.14
q-ign, J	.95	.97	1.06	1.06	1.01
q-decomp HNO_3, J	15.65	15.51	16.06	15.32	15.19
q-WC, J	5.40	5.07	5.27	5.17	5.06
q-corr to 26 °C, J	.01	.00	.00	.00	.00
Q-std react, J	−2784.43	−2620.48	−2725.66	−2671.22	−2618.88
m_s, g	.240709	.226561	.235644	.230945	.226476
ΔU °C (26 °C), J·g^{-1}	−11567.60	−11566.32	−11566.89	−11566.48	−11563.57
Mean, ΔU ° (28 °C), J·g^{-1}	−11566.17				
sdm	±.69				

Table 10. Results of the Triazine V combustion experiments.

Expt. No.	167	168	169	170	171	362
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85	2517.46
Cv-cont(i), J·K^{-1}	11.93	15.93	16.00	15.97	16.00	15.93
Corr to tm, J·K^{-1}	−.03	−.06	.01	.02	−.01	−.02
Corr-parts, J·K^{-1}	.00	.00	.00	.00	.00	−.08
EEE-actual, J·K^{-1}	2526.75	2530.77	2530.86	2530.84	2530.84	2533.30
Temp rise, K	1.180365	.941348	1.007736	1.019433	.994826	.993761
Q-total, J	−2982.49	−2382.34	−2550.44	−2580.02	−2517.74	−2517.49
q-ign, J	.86	.95	.92	.90	1.02	.61
q-decomp HNO_3, J	13.85	14.25	15.71	15.42	16.34	15.41
q-WC, J	6.29	5.70	6.06	6.11	5.99	5.97
q-corr to 26 °C, J	.01	.00	.00	.00	.00	.00
Q-std react, J	−2961.48	−2361.45	−2527.74	−2557.59	−2494.40	−2495.50
M_s, g	.339291	.270904	.290118	.293462	.286357	.286325
ΔU°C (26 °C), J·g^{-1}	−8728.45	−8716.90	−8712.79	−8710.23	−8715.23	−8715.63
Mean EEE-std, J·K^{-1}	−8716.63					
sdm	±2.53					

Table 11. Results of the Triazine VI combustion experiments.

Expt. No.	201	203	204	205	206
EEE-Std, $J \cdot K^{-1}$	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), $J \cdot K^{-1}$	15.93	15.94	15.96	15.98	15.96
Corr to tm, $J \cdot K^{-1}$	−.04	−.02	.01	.06	.04
Corr-parts, $J \cdot K^{-1}$	.00	.00	.00	.00	.00
EEE-actual, $J \cdot K^{-1}$	2530.74	2530.77	2530.82	2530.90	2530.85
Temp rise, K	.959145	.979893	1.002171	1.071997	1.027877
Q-total, J	−2427.35	−2479.88	−2536.32	−2713.12	−2601.40
q-ign, J	.88	.78	78	.90	.86
q-decomp HNO_3, J	15.12	14.27	15.34	18.37	17.49
q-WC, J	6.04	6.18	6.33	6.74	6.45
q-corr to 26 °C, J	.00	.00	.00	.00	.00
Q-std react, J	−2405.32	−2458.65	−2513.86	−2687.11	−2576.61
m_s, g	.298999	.305657	.312668	.334324	.320487
ΔU °C (26 °C), $J \cdot g^{-1}$	−8044.57	−8043.82	−8040.03	−8037.42	−8039.67
Mean, ΔU ° (28 °C), $J \cdot g^{-1}$	−8041.10				
sdm	±1.34				

(2) 2,4,6-Triethoxy-1,3,5-triazine **Triazine II**
$C_9H_{15}O_3N_3(c)+11.25\ O_2(g) \rightarrow 9\ CO_2(g)+1.5\ N_2(g)$
$+7.5\ H_2O(liq)$
$\Delta U\ °C(26\ °C)=-23909.2 \pm 6.7\ J/g$

(3) 2,4,6-Tris(2-fluoro-2,2-dinitroethoxy) -1,3,5-triazine **Triazine III**
$C_9H_6O_{15}N_9F_3(c)+2.25\ O_2(g)+298.5\ H_2O(liq)$
$\rightarrow 9\ CO_2(g)+4.5\ N_2(g)+3[HF+100\ H_2O](liq)$
$\Delta U\ °C(26\ °C)=-7177.4 \pm 2.9\ J/g$

(4) 2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy) -1,3,5-triazine **Triazine IV**
$C_7H_8O_7N_5F(c)+5.25\ O_2(g)+96.5\ H_2O(liq)$
$\rightarrow 7\ CO_2(g)+2.5\ N_2(g)+[HF+100\ H_2O](liq)$
$\Delta U\ °C(26\ °C)=11566.2 \pm 4.9\ J/g$

(5) 2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine V**
$C_8H_7O_{11}N_7F_2(c)+3.75\ O_2(g)+197.5\ H_2O(liq)$
$\rightarrow 8\ CO_2(g)+3.5\ N_2(g)+2[HF+100\ H_2O](liq)$
$\Delta U\ °C(26\ °C)=-8716.6 \pm 5.6\ J/g$

(6) 2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine VI**
$C_7H_6O_{10}N_8F_2(c)+3\ O_2(g)+198\ H_2O(liq)$
$\rightarrow 7\ CO_2(g)+4\ N_2(g)+2\ [HF+100\ H_2O](liq)$
$\Delta U\ °C(26\ °C)=-8041.1 \pm 2.4\ J/g$

The enthalpies of combustion have been combined with the enthalpies of formation of carbon dioxide [19], water [19], and aqueous hydrofluoric acid [20] to obtain the enthalpies of formation. A summary of the experimental heats of combustion and the derived values for heats of formation is given in table 12.

Table 12. Summary of the experimental and derived values.

Convenient Name	Chemical Name	ΔU °C (26 °C) kJ/mol	ΔH °C (25 °C) kJ/mol	ΔH °F (25 °C) kJ/mol
Triazine I	2,4,6-Trimethoxy-1,3,5-triazine	−18524.30±0.26[a]	−3168.69±.83	−478.60±.87
Triazine II	2,4,6-Triethoxy-1,3,5-triazine	−23909.24±1.56	−5100.31±1..43	−584.99±1.50
Triazine III	2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−7177.40±0.62	−3827.60±1.21	−1109.80±1.53
Triazine IV	2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−11566.17±0.69	−3380.24±1.00	−697.08±1.15
Triazine V	2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−8716.63±2.53	−3599.66±2.30	−907.71±2.40
Triazine VI	2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−8041.10±1.34	−3197.82±1.36	−773.12±1.50

[a] Actual temperature 28 °C for Triazine I.

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Metrics and Techniques to Measure Microcomputer Productivity

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While it is generally assumed that the use of microcomputers helps to improve productivity in an office environment, quantitative measures in this area are lacking. This paper addresses the measurement of the effect on productivity in an end user, office environment as a result of the introduction of micrompúter-based technology. It is concerned with defining how productivity can be measured in such an environment and with current efforts to measure changes in productivity. It identifies and assesses the various techniques and measures used to describe the magnitude of productivity improvements that result from the use of microcomputers in the workplace, and makes recommendations for ways in which changes in productivity, may be measured.

Key words: added-value; automation; efficiency, measure; methodology; metrics; microcomputers; office enviornment; productivity; qualitative measurement; quantitative measurement.

Introduction

The role of information processing has changed with the introduction of the microcomputer into the workplace. The microcomputer has become a "tool" that often enables the user to directly control information processing needs without the assistance of the professional ADP staff. The relative low cost of microcomputers, their adaptability to various applications, and the availability of software which is useful to noncomputer professionals has resulted in the proliferation and use of microcomputers in the office environment.

While there is general agreement that microcomputers do increase office productivity, there is little hard, quantifiable data to actually support this claim. Many companies have published reports of substantial improvements to productivity, but few have attempted to actually measure the changes, and fewer still have achieved any reliable measurements. By and large, the published reports have drawn the conclusion of productivity gains based on the perception of the managers and workers in the affected office environments.

The use of microcomputers by professional and clerical staffs overlap but are functionally different. The clerical staff primarily utilizes word processing which can be measured at the individual level (e.g., number of words in within a specific period). It appears, however, that the primary benefits to the professional staff are not in speeding up the information flow, but in improving the depth of analysis and understanding of the available information. Therefore, professional staff productivity should be measured in terms of the information handled and processed. Through spread sheet analysis and accounting and financial systems, the professional can better understand the significance of the information and

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thus, can make more informed decisions which result in improved performance of the entire organization.

This paper addresses the measurement of the effect on productivity in an end user, office environment as a result of the introduction of microcomputer-based technology. It analyzes and assesses the various measurement techniques presented and makes recommendations on how to measure productivity gains in the functional workforce. Measuring productivity changes in an office environment primarily involves the assessment of the impact of new technology on qualitative factors which cannot be measured directly. Thus, the inability to assign a numerical value to a factor such as "efficiency" limits the measurement and makes it highly subjective. In general, if the product or service is completed faster; if the quality and performance is improved; if there are noticeable, desirable differences in the process; then there are productivity gains for the organization.

Productivity is often equated with efficiency (reducing unit costs, improving output per hour, reducing errors, etc.) or quantity of work performed. Quality of output may, in fact, be far more important than quantity when measuring and assessing traditional white collar worker performance since accurate communication of information is the primary function of such workers. The usefulness and effectiveness of this output is determined by such qualitative characteristics as "efficiency," "completeness," and "effectiveness." Although these attributes are discernible to those involved, they are not directly measurable and thus, an assessment of changes in productivity is much more difficult to make. Productivity measurement can be facilitated if the input properties and the output properties are clearly defined. This is more difficult to do in a white collar environment since most managerial and professional work does not have well-defined, measurable inputs or well-defined outputs. Thus, the usefulness of any productivity measurement is dependent upon the accuracy of the perceptions of the qualitative factors which are used.

The introduction and use of microcomputers have increased the productivity of users, but measuring these increases has not been easy. Much of the difficulty is due to the fact that techniques for measuring productivity are neither well-known nor well-defined. Further, the benefits do not always appear as single, discernible entities, rather they are often small gains across many tasks. As a result, few organizations have initiated productivity measurements citing the lack of money, time, knowledge, or an inclination to perform a comprehensive, scientific study. The situation is further complicated by the lack of information needed to measure productivity.

One of the perennial problems is the difficulty in measuring the productivity of value-added activities. Inevitably when a manual system is automated, many new functions and products are generated, usually without additional resources and at negligible cost. These intangible byproducts of automation,which did not exist previously, can enhance a manager's decision making ability. Another problem in measuring productivity gains is the omission of some of the cost of converting from manual to automated methods, and a comparison of these costs against the benefits. Some of the costs typically omitted are site preparation, training, and ongoing software maintenance. Quantifying professional or managerial productivity has proven to be difficult, particularly for such activities as: preparation for and attending meetings, reading and writing reports, responding to telephone calls, etc.

Prior to implementing a productivity measurement program, there are a number of factors to be considered. While the methodology (presented in table 5) is recommended for measuring changes in productivity, it may not be feasible depending on organizational constraints. These constraints include:

- the unavailability of measurement data/information. It is difficult to measure changes in productivity in the absence of baseline data. If the information needed to conduct such a study is incomplete or unavailable it may be better to rely on the judgement of the users of the microcomputers.
- the lack of well-defined productivity measurement techniques. Measures of productivity that are appropriate for the different levels and functions in the organization must be well-defined.
- the cost, time, and effort to effectively measure productivity.
- the lack of a means to capture much of what is done in an office environment.
- the size of the organization or project, and the type of applications. If the environment is small, the cost of such a study could outweigh the benefits.
- the lack of (active) participation in the productivity measurement program by all impacted by the introduction of microcomputer.

Once the decision has been made to measure changes in productivity, it is often desirable to implement a productivity improvement program to maximize productivity gains resulting from microcomputer use.

Quite simply, organizations are as concerned with what a productivity program is going to cost as with what it is going to return. Knowing how to spend funds where the most benefit can be realized, however, is sometimes difficult. Before productivity can be effectively measured, there must be a thorough understanding of what is being done, the activities performed, for whom, and why. While the old maxim, "you can't improve what you can't measure" is not entirely true, it is important to develop a strategy for defining what to measure, when to measure, and how to use the measurement data.

As the activities performed in the functional workplace become more complex and technical in nature, and ready access to reliable information becomes more critical, it is essential to make better use of each individual's time. The effectiveness of any productivity measure is how accurately it reflects what is taking place with respect to the ability of the individual, and ultimately the organization, to perform tasks easier, faster, and better.

Measuring Changes in Productivity

Techniques for measuring changes in productivity rely on two types of measurements: quantitative and qualitative. Quantitative techniques generally measure quantities of work over some unit of time such as "pieces per hour," "person-hours per completed product," or "defects per unit of time." These types of measurements are fairly easy to quantify and are typical of measurements made when investigating productivity changes in a production, blue-collar environment. Qualitative techniques are those which address less tangible attributes such as "quality," "effectiveness," and "efficiency." Measurement of such attributes is very difficult because it is highly subjective.

Assessing productivity and changes resulting from the introduction of microcomputers primarily requires the measuring or estimating of qualitative attributes rather than quantitative factors. While it is not possible to obtain highly definitive qualitative measurements, it is possible to assess the relative changes in productivity through a careful and consistent assessment of selected qualitative attributes before and after the introduction of the new technology.

Measuring changes in productivity can be done at the global (organization), local (functional unit), or individual level. Measurement of quantitative factors can be successfully performed at the lowest individual levels since exact counts can be obtained for specific factors (number of letters typed, hours worked, number of forms processed, etc.). Assessment of qualitative attributes, however, is more reliable at a higher level within an organization since the individual variances and inconsistencies will tend to balance out.

Based on the literature search which was conducted as part of this task, there is a great deal of interest in productivity measurement in general and the effects of microcomputers on productivity in particular. This literature search included more than 200 sources, of which 47 appear at the end of this paper as a selected bibliography. Many organizations have initiated efforts to determine the effects of microcomputers on individual and organizational productivity. However, there is a dearth of information on any actual quantifiable changes. These reports consistently discuss the difficulties in performing such measurement and usually conclude that there has been improvement in productivity on a global level as a result of the introduction of microcomputers.

Some of the techniques discussed later in this section have been proposed to provide quantifiable measurements. Organizations have been reluctant, however, to embark on the effort required to make such measurements citing the cost, lack of time, lack of information, and lack of proof that these techniques will actually provide useable results. Thus, the consensus is that microcomputers have improved productivity, but there is little actual documentation to support that conclusion.

What Should be Measured

Productivity measurement, particularly of qualitative items, can be a costly endeavor. In a small organization with limited resources, it may be unreasonable to undertake a comprehensive study either to determine productivity gains or to determine how achieve to them. Regardless of the size of the organization, it may be determined after a careful evaluation of organization goals, objectives, and requirements that the difficulty of implementing a productivity measurement program just would not be cost effective. Another instance in which a program to measure changes in productivity may be unnecessary is when it is *obvious* that the use of microcomputers has resulted in improved productivity.

The attributes and factors to be measured must be selected and carefully defined. Since each organization is unique, the attributes and factors selected for measurement will differ. After the technology has been introduced, sufficient time should transpire before conducting the second productivity measurement. This is important because there may be a short-term decline in productivity which occurs while the users are learning to use the new technology properly. The baseline and new productivity levels should then be carefully evaluated and an assessment made on the relative productivity changes which have been realized.

Factors that complicate measurement. Several factors frequently complicate the measurements:

- Value-added activities may not be adequately measured. When a manual system is automated, many new functions and products may be generated without requiring additional resources or cost. These activities, while difficult to measure, should be taken into consideration.
- A number of cost factors are frequently omitted when measuring productivity gains. Included are those costs associated with the conversion from manual to automated procedures such as: site preparation, training, and maintenance of both the hardware and the software systems.
- The introduction of new technology frequently results in substantial changes to the office environment. *Personnel become responsible for different* or additional parts of the process, duties shift, and some work may be eliminated while new work is created. Thus, attempts to measure individual productivity changes is often a case of comparing apples and oranges. For this reason, the assessment should be made at the organizational level rather than the individual level.

Factors and attributes for measuring productivity. The following three tables list some of the more commonly used factors and attributes used in evaluating productivity. Table 1 identifies tangible, quantitative factors which can be measured directly. Table 2 and table 3 identify less tangible, more subjective, qualitative attributes which should be assessed in attempting to evaluate the productivity of an organization. Section three provides a discussion of several case studies which make use of many of the factors and attributes identified in the tables below.

Table 1. Factors that can be measured and quantified to determine productivity gains.

- workload
- schedules
- cost/budget
- end products
- training cost
- size of staff
- methods/techniques
- response/turnaround time
- time to perform a specific task
- number of new requests/alternatives examined
- outputs before and after using microcomputers
- amount of data handled, sorted, and calculated

Table 2. Attributes which can be measured but not easily quantified to assess productivity gains.

- accuracy
- efficiency
- reliability
- completeness
- user acceptance
- data accessibility
- value added capabilities
- improved analysis (budget, trends, etc.)
- timeliness of reports/tickler files/information

The productivity improvements most frequently mentioned as a result of using microcomputers are increased workload, new or more work accomplished in a shorter time, and cost saving. Improved accuracy, efficiency, quality, attitude and morale are also cited as benefits of microcomputer use. Not all of factors and attributes identified may be appropriate to a specific situation, while others not found in these tables may be critical in specific environments.

Criteria to measure desired outcomes. The ultimate objective of introducing microcomputers is to increase the productivity of an organization. This may be accomplished by reducing costs, avoiding increases in costs, increasing value added activities/products, increasing employee satisfaction or becoming more competitive. Our findings indicate that the identification of desired outcomes and the selection of appropriate measurement criteria are essential to the success of any productivity measurement program. The desired outcome, more than any other factor, influences the choice of criteria for measuring the outcome and determining if goals have been achieved. Table 4 identifies some possible criteria for different objectives and goals.

Measurement Techniques

Measurable improvements in productivity generally can be attributed to a combination of human resource and technological factors. Therefore, any effort to determine changes in productivity as a result of the introduction of microcomputers should consider both the work environment (equipment and tools) and the employee effectiveness (training, education, attitude).

There are few effective measurement techniques available for measuring productivity in the office envi-

Table 3. Attributes which are not easily measured nor quantifiable to determine productivity gains.

- control
- flexibility
- communication
- attitude and morale
- quality of decisions
- new insights and learning
- better understanding of business
- effectiveness (of team work, etc.)
- quality of presentations (graphic displays, etc)

Table 4. Criteria to measure desired outcomes for OA projects.

Desired Outcome	Possible Criteria
To increase organizational productivity	Total output in number of units produced as a function of labor, investment, etc. measured in dollars
To reduce or avoid costs	Cost of labor, materials, and overhead
To increase value-added with products/services	Contribution to profits from improved products/services
To increase managerial productivity	Time required to complete tasks and level of individual, unit, and organization productivity
To increase timeliness of information	Average and variance of time to prepare/distribute information
To increase quality of information	Quality, accuracy, and completeness of information used to generate products
To provide more job satisfaction	Turnover or absenteeism

ronment. The qualitative measurements which are most useful in assessing changes in the office productivity are most difficult to obtain. The quantitative measuring techniques can be characterized as a comparison of INPUT/OUTPUT before and after microcomputers are used. Although the INPUT is generally well-defined, the difficult aspect in performing this type of measurement in the functional workplace is quantifying the OUTPUT.

The most commonly used techniques for measuring changes in productivity are Questionnaires and Empirical Analysis (see table 5). The primary difference between these two approaches is that the latter relies more on intuitive knowledge and information gained through experience and less on a systematic, structured methodology. Both of these techniques make use of before and after information concerning the qualitative and quantitative aspects of the process and the products; both are relatively easy to employ; both can be administered formally or informally; and both can be used for almost any size and type of environment/organization.

Table 5. Productivity measurement techniques.

Questionnaire/Survey	Empirical Analysis
- Before and after[1] measurement	- Before and after measurement
- Assessment of need	- Intuitive
- Quantitative metrics	- Quantitative metrics
- Qualitative measures	- Qualitative measures
- Methodology/formula	

[1] The establishment of a baseline level of productivity prior to the introduction of the new technology is essential to the success of a "before and after" assessment.

Questionnaire technique. The questionnaire/survey method of assessing changes in productivity resulting from the introduction of microcomputers appears to be one of the most useful. One of the advantages provided by the technique is that it can readily be adapted to measure global, as well as localized changes in productivity. The questionnaire can be used to gather information about characteristics and functions of the organization; projected requirements and desired features; work process, equipment, and products; and profile data on individual performance. It can also be used to isolate problem areas, determine employee attitudes, and solicit suggestions.

Another advantage provided by the questionnaire/survey method is that it can be used to obtain information from multiple levels of the organization. This approach makes it possible to obtain information about perceived qualitative, as well as quantitative changes in productivity. This is essential since the perceptions of the changes may differ. In fact, everyone who either uses microcomputers, or is impacted by changes in the environment as a result of their use, should be surveyed. Properly employed, it is one of the most effective techniques for obtaining, comparing, evaluating, and measuring changes in productivity within the organization.

Empirical analysis measuring technique. Empirical analysis is employed to measure productivity before and after the introduction of microcomputers in the workplace. Empirical analysis relies primarily on experience and observations about a particular area or environment, and does not generally make use of systematic methods or methodologies. It may be performed by weighing and measuring the applicable, quantitative or tangible factors such as those identified in table 1. The weights are generally assigned to the variables to be measured based on the value and function of that variable within the specific environment. Qualitative factors may also be taken into consideration. Using empirical analysis, a baseline is established against which all changes are measured.

Recommendations on measurement techniques. When using either the questionnaire or the empirical analysis technique to measure productivity, it is important to focus on the extent of productivity changes at the global level, as opposed to the short term or incremental increases at the local level. The introduction of any new technology involves a learning period during which there may actually be a decline in productivity. Consequently, sufficient time must be allowed after microcomputers are introduced into the organization to permit a stable state of operation to be established before the productivity impact is assessed. The usefulness of these techniques is dependent upon the accuracy and completeness of the information collected, and the skill and knowledge of the surveyor or evaluator.

Table 6 contains a set of recommended steps which should be followed in measuring productivity changes in an office environment.

Methodology for Measuring Productivity

There are a number of approaches for determining a methodology for measuring productivity changes. One approach is to evaluate attempts by other organizations to measure productivity, while another is to determine the estimated cost of such a program, and then compare this cost with the expected gains in productivity. Whether or not either of these methods are employed, it is essential to determine the goals or desired outcomes of a productivity measurement program for the specific office environment. See table 4 for some desired outcome measurement criteria.

Preparing to measure change. The first step in preparing to measure changes in productivity after defining the goals is to determine the feasibility of such a program. This requires that those involved have a thorough understanding of what is meant by productivity, of the activities to be measured, and of the areas likely to benefit most from the application of productivity measures. Since productivity has different meanings in different environments, it is essential to establish a definition that is suitable for the environment that is to be measured.

Each environment is unique and the attributes and factors useful in one may not be appropriate for another. This is especially true in the case of qualitative, subjective attributes such as reliability, accessibility, and efficiency. Therefore, it is necessary to define not only a set of factors and attributes (productivity indicators), but a method for quantifying the qualitative attributes. It is also essential that changes in productivity be measured at the global or organizational level, as well as the local or individual level to ensure the least amount of bias. If there is little or no assurance that a program to measure changes in productivity can be justified from a budgetary standpoint, the costs are likely to outweigh the gains. Finally, if it is determined that the implementation of such a program is not feasible, then planning should cease.

Performing Measurements. Once the decision has been made to proceed, it is essential to establish and measure the baselined activities before and after microcomputers are introduced. After a sufficient time has elapsed, there should be a careful assessment and evaluation of any changes in productivity. This process should be repeated over a period of time at unscheduled intervals at sufficiently high levels within the organization to preclude constraints and otherwise, unrepresentative conclusions. Table 6 describes a methodology for both preparing for and performing productivity measurements.

Case Studies

As part of our study, we surveyed a number of organizations to determine their experiences in measuring productivity. We found that:

- Virtually every organization reported substantial gains in productivity.
- Most organizations and studies which reported gains in productivity from the use of microcomputers based that claim on a perceived improvement and the *subjective judgment* of management.
- Actual, quantitative measurement studies were either not conducted or did not yield quantifiable results.

Table 6. Steps in measuring changes in productivity.

A. Planning and Preparing to Measure Change
1. Determine the feasibility of measuring productivity changes in the specific environment.
2. Develop a definition of productivity for the specific organizational environment.
3. Identify the attributes to be used in measuring productivity and define a method of quantifying the subjective qualitative attributes.
4. Develop and implement productivity measures at the global or organizational level rather than at an individual level to ensure a reliable assessment.

B. Performing Measurements
1. Perform a measurement to establish the baseline productivity level.
2. Introduce the new technology.
3. Permit a sufficient period of time to elapse to allow any short term decreases in productivity to be eliminated.
4. Re-measure the productivity levels.
5. Carefully evaluate the results to ensure that the results are interpreted within the context of the organizational environment. The evaluation should be performed at the highest, global level possible to avoid local aberrations and biases.

This section presents the findings of eight case studies. Five of these are based on reports which are listed at the beginning of each case study, and three on information obtained directly from the organization. Table 7 provides a matrix which identifies the factors and attributes referenced in each of the following case studies.

While these eight case studies provide some insight on the different approaches used to determine changes in productivity, they demonstrate the difficulty in identifying and measuring subjective attributes. Each of the case studies reference increased workload, new or more work accomplished in shorter time, and cost saving as a result of using microcomputers. In many environments, microcomputers are credited with increasing productivity if schedules are met in a timely manner, if the workload is handled without additional staff, and if the products are acceptable and of high quality without the benefit of any "formal" measurements. Table 7 lists factors or indicators identified in the selected case studies:

As indicated, very little quantitative data is available and most of the conclusions of improved productivity are based on intuitive belief, not on firm, scientific measurement.

Table 7. Case Study Matrix.

Firm	Table 1 Factors Measured	Table 2/3 Attributes Assessed
1. NSRDC	workload staff time etc.	timeliness efficiency quality
2. GAO	workload manpower cost number hours data handled	improved analysis efficiency
3. GSA	manpower cost workload etc.	qualitative benefits timeliness, etc.
4. USS	costs workload etc.	users/mgrs. best judge of how much productivity is achieved (no detail)
5. American Productivity Center Bethlehem Steel		improved morale timeliness communication reliability (errors reduced) quality of life teamwork
Polaroid	costs workload	
6. Banking	cost	
7. Data Processing and Research	workload time	value-added capabilities
8. Brokerage Firm	cost	user acceptance

1. Naval Ship Research And Development Center

Van Eseltine, R.T., "The Scientific/Engineering Workstation Experiment: Plans and Progress," *Proceedings of the 22nd Annual Technical Symposium of the Washington, DC, Chapter of the ACM*, Co-sponsored by the National Bureau ofStandards, June 1983, (Questionnaire and Empirical Analysis)

As part of the Technical Office Automation and Communication (TOFACS) project, the David W. Taylor Naval Ship Research and Development Center has undertaken a study of the effects of individual scientific/engineering workstations (SEWs) on the productivity of scientists and engineers. A prototype network of SEWs was developed to assess the changes in productivity which could result from the introduction of SEWs. Initial results of this research indicate that workstations are viable tools which aid productivity in a scientific and engineering environment.

The technique used in this study was to have the subjects being studied perform the evaluation and assessment of their before and after productivity levels for a brief description of the methodology employed. A rather complex formula was used which basically involved applying values to attributes before and after the introduction of the workstations, and then calculating the change in the ratio of the Output to Input totals. Quantitative data was gathered by having the technical staff assess the changes in how long it took to complete a typical task with and without the scientific and engineering workstation. Most of the other data was more subjective (qualitative) in nature and less easy to quantify. The use of the subjects to evaluate their changes in productivity resulted in more consistent assessments on an individual basis, but may have also introduced biases which could affect the findings. In general, this method appeared to work satisfactorily in this R&D laboratory environment and the general methodology could be applicable to other similar measurement attempts.

2. General Accounting Office

"Workstation Project Report To Information Policy Committee," Directed by Kenneth Pollock, Associate Director of Information Management Systems, General Accounting Office, Internal Study, 1982. (Questionnaire)

The GAO initiated an electronic workstation project to determine if the installation of workstations "could be cost effective at GAO in performing various auditor functions." The auditing (workload) functions are described and activities are divided into categories for the purpose of measurement. Benefits and problems are discussed. A matrix of automatable and non-automatable activities was defined and provided the basis for determining how best to utilize the workstations.

This report discusses the study and the methods employed *and concludes that an approximate 25% increase* in the capacity to perform audit functions was realized as a result of the introduction of the electronic workstations. The basic measurement unit utilized was the number of staff hours actually needed versus the estimated number of hours which would have been required if the electronic workstation had not been introduced. The report contains little information on the actual collection and analysis of data.

3. General Services Administration

"Final Report on the GSA End User Computer Pilot Project," Prepared by The General Service Administration's End User Computer Support Staff (KGS-1), September 28, 1983. (Empirical Analysis)

The General Services Administration conducted a pilot project to study the effects of the introduction of microcomputers within GSA. The project involved 500 GSA employees using 53 microcomputers and consisted of the automation of 175 applications. The report provides information on the experiences during the project and identifies the actions completed or initiated to facilitate end user computing. The report summarizes both the qualitative and quantitative benefits encountered by the end users. Most improvements were a result of automating manual operations. Specific examples of productivity gains are given in terms of cost savings, manhours, and increased workloads/tasks.

In discussing the findings, the report notes that in some cases productivity increases were measured "in terms of staff hours, or dollars," but in others they were not quantifiable because "the microcomputers satisfied requirements that were previously postponed due to staffing shortages." Direct changes in productivity were measured in terms of changes in staff hours or dollars whenever possible.

However, most of the conclusions drawn in this report are based on qualitative estimates of perceived improvement to the process. Nevertheless, there is a very strong indication that "the use of microcomputers can pay for themselves in less than one year" and can "help provide better, more timely products and more in-depth analysis."

4. United States Senate

"The Pilot Test of Office Automation Equipment in the Offices of United States Senators," Committee on Rules and Administration United States Senate, S-Prt 98-120, November 1983. (Questionnaire, Empirical Analysis, and Before/After Measurement)

This pilot study focused on office automation in the U.S. Senate offices. The method used to measure productivity gains was a before and after analysis of the functional requirements and the day-to-day office workload. Participants were asked to complete forms which identified the areas that could be improved most by automation. They were also asked to rank each of the areas in terms of importance to the performance of their responsibilities. Guidelines were developed to ensure that everyone recorded the same types of information in assessing changes as a result of automation. The key aspect of the productivity measurement program was the requirement that productivity goals and cost justification be established for each workstation to be installed.

The test demonstrated that the staff could quickly learn to use the equipment and put it to productive use. The report does not present any detailed information on measuring productivity changes but does state that "in the final analysis, the actual users and office managers are the best judges of how much improvement has been achieved."

5. American Productivity Center

Steel, "White-Collar Productivity: The National Challenge and Case Studies," sponsored by Steelcase Inc., Grand Rapids, Michigan, 1982. (Questionnaire and Empirical Analysis)

Steelcase Inc. commissioned the American Productivity Center, a nationally recognized expert on productivity issues, to conduct a study on productivity in the workplace. During this six month study, the Productivity Center sent survey questionnaires to 600 U.S. firms and received 140 responses. The study is based on those responses and includes 25 case studies selected on the basis of the techniques used to assess and measure productivity gains resulting from the introduction of office automation. While this study does not identify any unique measurement techniques, it does suggest that almost any productivity improvement program, no matter how unstructured, can result in increased productivity.

Word processing was found to be the most effective factor in improving office productivity. Other factors consistently cited were team building and the work environment. The productivity measurement programs of two of the most representative case studies are described and evaluated below:

a) Bethlehem Steel (Methodology/Intuitive). Bethlehem Steel initiated a Productivity through Office Systems (PROS) effort to improve productivity of the 400 person sales force and their support personnel. The thrust of PROS, which was aimed at the secretarial force, involved the introduction of both an office automation system and a "Quality of Work Life" (QWL) methodology. The QWL methodology program encourages greater employee participation, and provides for training in all aspects of an office that contribute to the "quality of life" in the office. As part of this effort, monthly PROS meetings were held to address team building, problem solving, and other issues which can strengthen employee capabilities. No formal techniques or measurements were undertaken either before or after the office automation system was installed. There is a strong perception, however, that there were substantial gains in productivity which could be attributed to both office automation and to the QWL methodology program. The reported subjective estimates of the productivity improvements were:

• increased output	20%
• more timely delivery	80%
• credibility of offices	20%
• morale improved	20%
• task difficulty reduced	20%
• communication improved	50%
• space more effectively used	25%
• response time reduced	80%
• errors reduced	5%
• quality of service enhanced	50%

b) Polaroid (Needs Assessment). Polaroid, spurred by a reduction of 4000 employees between 1978 and 1982, established an Office Technology Council to determine how to "better manage and utilize emerging office technologies, reduce cost and enhance the effectiveness and productivity of personnel." As a first task, the Council developed and implemented a seven-step "Needs Assessment Methodology" to justify the acquisition of new technology. An examination was made of the personnel, workload, and tools needed within the organization to accomplish its mission; data was gathered and evaluated; and a summary of the qualitative benefits expected from the application of electronic technology was made. Polaroid considers this type of assessment helpful in identifying methods for improving productivity prior to the introduction of new technology. The seven steps of the methodology are:

a) Orientation (Overall mission, functions, needs, equipment, costs)
b) Professional activity profile
c) Administrative profile
d) Administrative reporting
e) Detailed workload
f) Word processing benefits summary
g) Financial Analysis worksheet

6. Banking (Empirical Analysis)

A large northeastern bank is currently using 75 microcomputers for such varied applications as: budget and financial analysis, gas and oil studies, balance sheet reporting, and custom tailored accounts. Although a formal study has not been conducted, this firm believes that significant gains in productivity have been achieved and that microcomputers have proven to be very cost effective.

7. Data Processing and Research (Empirical Analysis)

A large data processing firm provides service for the 50 major U.S. banks in the country. Some of the applications handled by the firm include: a significant amount of file transfer—from micro to mainframe; extensive word processing; budget analysis; and value added processing. A much greater workload (volume of transactions) is now being handled in a shorter period of time due to the use of microcomputers. No formal study has been conducted, but it is accepted by the firm that the use of microcomputers has resulted in increased productivity.

8. Brokerage Firm (Empirical Analysis)

A large New York brokerage firm makes extensive use of microcomputers to handle customer accounts around the country. While no formal studies have been undertaken, customers have indicated that the use of microcomputers generally results in productivity gains and that the replication of successful microcomputer applications would increase both productivity and cost effectiveness. Overall, this firm has been successful in the introduction of microcomputers. However, concerns were expressed that there may not always be sufficient control and coordination of this process.

As stated in the introduction to this section, two distinct conclusions can be drawn from the available information on the measurement of the effect on productivity from the introduction of microcomputer-based technology into the office environment.

- Nearly everyone claims to have obtained significant improvements in productivity.
- Virtually no one has successfully measured and quantified those changes.

There is strong, anecdotal, circumstantial evidence that most of the claims of increased productivity are correct. There is, however, little reason to accept the specific percentages which are cited. Nevertheless, the strong perception of improved productivity has been sufficient to justify the further acquisition of microcomputers in many organizations.

Improving Productivity: Management Considerations

Once the meaning of productivity is understood, the next step is to ensure that the environment is conducive to the performance of high quality work, and that the responsibilities for a high level of productivity are well-defined. Individuals should have a clear understanding of their job responsibilities and should be held accountable for results. They must be made to feel that they make a difference. If productivity is a major organizational concern, then the individuals within the organization must also be a major concern. This implies that there must be a feeling engendered among the workers that they are: valued, trusted, challenged, making a contribution, and involved in decisions affecting them.

Increases in productivity and profitability, however, cannot be achieved simply with acquisition of new and better technology. Such acquisitions should be accompanied by a management commitment to implement a cost-justified, strategic, system integration approach which addresses the human or social aspects of automation on both the individual and the organization. Too often, productivity has little or no meaning for the individual since it is viewed as an attempt by management to impose more procedures and controls, and ultimately, more work with little additional remuneration. There is likely to be little incentive to use new tools and techniques or to improve performance, if a feeling exists that productivity measures are only being taken to increase the organization's image or profits at the expense of the worker.

Improvements in productivity require upper management to play an active role in the productivity improvement program and also requires that the affected individuals realize benefits from the changes. The introduction and use of microcomputer and related hardware and software must be accompanied by proper and adequate training and regard for the individual's working environment.

In order to achieve significant productivity gains, there must be an integrated, cost-justified, program designed to achieve improvements in predefined areas which would benefit most by the improved productivity. The areas most frequently cited as being in need of improvement are: management, incentives for individuals, work environments, tools, training, software quality and software maintenance. Therefore, the initiation of a comprehensive productivity improvement program can be both a costly and long term effort which requires careful *planning, coordination*, and the *cooperation* of all concerned.

It is essential to plan for some recognizable gain within the first two years, substantially more within the next two or three, and depending upon the extent and cost of the effort to achieve an increase in productivity, there should be still more gain within the next five years. A well-planned productivity program should have a substantial payoff within three to ten years.

Implementing a productivity program, however, is not without some risks. If it is not well-planned, there is likely to be excessive optimism and overestimation of potential productivity gains. If the efforts are not well-coordinated, there may be only spotty success, resulting in little overall benefit to the organization. If it is viewed negatively, the workers may decide to thwart its implementation, causing it to fail. And finally, unless there is cooperation between each level of management, professionals, clericals, end users, and others for whom the program is intended, there is little likelihood for success.

Table 8 outlines the basic steps which should be taken to establish a Productivity Improvement Program within an organization. Adherence to this program will help ensure that the measurement of changes in productivity, using the metrics discussed earlier in this paper will result in definite gains in productivity from the introduction of current technology into an office environment.

Summary and Conclusions

While no definitive techniques for measuring productivity changes in an functional workplace were identified, this study did find overwhelming support for the idea that the introduction of microcomputers to the functional workforce will result in significant improvements in productivity. The "measurement" techniques employed have usually been highly subjective and sensitive to biasing factors which can make the cited statistics highly suspect. The most that can be concluded is that microcomputers appear to increase productivity and that this perception is very widely held.

A few organizations have identified a set of measures unique to their environments. Some of these, as in the case of NSRDC, may be conceptually transferred to other environments. However, with the exception of traditional method of measuring inputs and outputs (before and after), there are virtually no universally accepted productivity measures for use in an office environment.

Summary

Our findings indicate that there are several key factors which should be clearly understood when attempting to evaluate and measure the productivity within an organization. These findings are summarized below:

- **Few Effective Measures**

The measurement of changes in productivity in a *production environment* is a well-understood process; however, the measurement of such changes in an office environment is much more difficult to quantify. While various methods have been proposed for measuring changes in productivity resulting from the introduction of microcomputers, very few are effective.

The useful measures are those which primarily address qualitative aspects of the environment and the work produced. These measures are highly subjective and thus, must also be evaluated in light of the methods and techniques used to produce the measurements.

- **Qualitative Measures Should Be Global**

Too often, an attempt is made to measure productivity at the atomic or detailed level. The introduction of microcomputers may affect how and what individuals in an organization do to varying degrees. Indeed, the actual work (throughput) of some individuals may appear to decrease. While this would seem to contraindicate the use of microcomputers in this case, an examination at a higher, macro level, may show that there has been a resultant overall improvement in productivity.

The key to a successful productivity improvement program is to define what is expected in terms of productivity gains, specifically, what and how to measure, and then proceed. The best measurements of productivity changes in an office environment are qualitative. These measures are the most accurate when employed at an organizational level. It should be clearly understood that the goal of any productivity program is to improve the overall productivity of the organization. Thus, the measurements should be made at the global level and indications of increases or decreases in productivity at individual levels should be evaluated within the context of the productivity changes of the entire organization.

- **Measurements Must Be Made Against an Established Baseline**

Results of measurement techniques can be highly suspect since the items being measured or counted are often subject to various conflicting interpretations. Regardless of the method or technique used, it is essential to measure changes in productivity against an established baseline. The questionnaire method appears to be the most useful in obtaining, comparing, evaluating, and

Table 8. Establishing a productivity improvement program.

1. Determine how the tasks/jobs are currently done.
2. Determine where performance can be improved.
3. Define the level of productivity gain expected.
4. Perform a cost-benefit analysis to determine if this is a feasible expectation.
5. Understand that introducing automation requires significant up front costs.
6. Take future inflation into account.
7. Determine the amount to be committed to achieve productivity gains.
8. Determine for whom equipment will be used. In white collar domains, there are clearly two sets of users: professional and clerical.
9. Determine for which applications equipment will be used.
10. Determine what kind of equipment will be used.
11. Evaluate large, difficult to maintain programs for possible replacement with off the shelf packages.
12. Evaluate activities that require substantial resources, i.e., OR, simulation, job scheduling, for possible replacement by more efficient ones.
13. Run a pilot to substantiate the expected improvements.
14. If the pilot is successful, go forward with the whole program.

measuring relative changes in productivity against a baseline. This method provides for gathering information on qualitative, as well as quantitative changes in productivity.

- **Allow Sufficient Time Before Measuring Productivity Changes**

The introduction of any new technology involves a learning period during which there may actually be a decline in productivity. On the other hand, the excitement of being involved in an "experiment," such as the introduction of microcomputers in an organization, may also lead to an increase in productivity. The effect, however, may be more pronounced immediately after the introduction of microcomputers than later. Consequently, sufficient time must be allowed after microcomputers are introduced into the organization to permit a stable state of operation to be established before the productivity impact is assessed.

- **Measurements Should Be Carefully Evaluated**

Improper or undisciplined use of microcomputers can be counterproductive due to the wrong work being done or to new work being created which is not needed. Thus, the measurement of the effects of microcomputer use should be carefully evaluated. Care should be taken to evaluate the impact on the entire organization, not just the directly affected individual. In addition, measurements must be made over a long enough time period to balance any short term drops or rises in productivity.

Microcomputer use within the organization decentralizes the computing resources and enables users (ADP professionals as well as those without previous ADP experience) to be in direct control of their information processing activities. The user has a wide range of information on which to base decisions and can make those decisions quickly and accurately. Consequently, the user can perform his job more efficiently and effectively. While microcomputers are frequently used as stand alone, general purpose tools, they are rapidly becoming a means of accessing the large scale systems and other microcomputers. The link between the microcomputer and mainframe provides the user with broader range of capabilities and greater potential for productivity gains. The result is the work being done faster, the quality of reports and other documents is improved, and work is performed which was previously not possible.

Conclusions

The primary purpose for measuring changes in productivity resulting from the use of microcomputers is to provide evidence of their cost-effectiveness and impact on the organization. This can be accomplished in a number of ways ranging from a cursory examination of activities and products before and after the introduction of microcomputers, to a plan which encompasses the recommended methodology outlined in table 6. We strongly recommend the use of this methodology to determine first, whether to initiate a measurement program; and secondly, how to go about performing the measurements.

A significant number of Federal Government and private sector organizations have introduced microcomputers and subsequently, have been able to identify gains in overall productivity. Although many of these organizations introduced microcomputers *without the benefit of a prior productivity measurement study or program,* evidence of their cost effectiveness and impact on the organization has come from both managers and end-users. The management of these organizations is convinced that improvements in products, services, efficiency, morale, and numerous other areas occurred as a result of using microcomputers.

Prior to initiating a study or program to measure changes in productivity, some consideration should be given to the feasibility and cost benefits of such a program. (see step 1 of table 6). If it is determined that a productivity measurement program is not feasible, or if there is little or no assurance that such a program could be justified from a budgetary standpoint, then it may be better to rely on the judgement of the managers and users of the microcomputers.

Therefore, while a study or program to measure changes in productivity as a result of using microcomputers may be a worthwhile endeavor, it is not necessary or appropriate for every environment.

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conference report

FIELD EFFECTS ON RYDBERG ATOMS

During the past decade the use of lasers to do detailed spectroscopic studies has led to an increased interest in the physics of atoms in which one electron is at a large distance from the atomic core. These "Rydberg atoms" are often extremely sensitive to applied electric (Stark effect) and magnetic (Zeeman effect) fields and field free spectroscopic studies have been complemented by investigations of the effects of such fields on Rydberg atoms. Basic research in this area has important practical applications. In particular, the process of dielectronic recombination, in which a free electron is captured by an atomic ion to form a Rydberg state which then emits radiation, is an important loss mechanism in fusion plasmas and is responsible for satellite lines observed in emission from astrophysical plasmas. The first laboratory measurements of cross sections for this important process have been made during the past several years, and the results of these measurements are apparently affected by the small fields present in the laboratory environment.

A two-day workshop on "Atomic Spectra and Collisions in External Fields" held at NBS on October 22-23, 1984 focused on recent experimental and theoretical developments in the general area of field effects on atomic systems and their importance in fusion research and astrophysics. The meeting was sponsored by the National Measurement Laboratory, the Department of Energy, the National Science Foundation, and the University of Illinois, and was international in scope with 14 of the 70 attendees from laboratories outside the United States.

The first day of the workshop included reviews of our current understanding of the Zeeman and Stark effects on Rydberg atoms presented by C. W. Clark (NBS) and D. A. Harmin (University of Colorado). New theoretical developments in Zeeman spectroscopy and in crossed field spectroscopy; i.e., with both electric and magnetic fields present, were discussed by H. S. Taylor (University of Southern California) and M. G. Littman (Princeton University). J. C. Gay (Ecole Normale Superieure, France) presented new results on group theoretical approaches to field effects on Rydberg atoms.

On the experimental side, new results on electric field effects on hydrogen, the atom for which the most extensive theoretical calculations are available, were discussed by M. H. Nayfeh (University of Illinois) and K. Welge (Universitat of Bielefeld, Fed. Rep. of Germany). Recent work on Stark effect measurements made at high fields using relativistic beams at the Los Alamos "Meson Factory" (LAMPF), as well as earlier measurements on negative hydrogen ions, were reported by W. W. Smith (University of Connecticut) and H. C. Bryant (University of New Mexico). Measurements on helium and sodium were described by P. Koch and H. Metcalf (both of State University of New York at Stony Brook) and S. Liberman reported on recent field effect studies and their interpretation at Laboratoire Aime Cotton (Paris, France). T. F. Gallagher (University of Virginia) discussed recent work on autoionizing states of barium reached by multi-step processes and their relationship to dielectric recombination, and R. Hulet (Massachusetts Institute of Technology) reported on the excitation of Rydberg atoms to states with large azimuthal quantum numbers using microwave techniques to produce atoms with practically circular orbits. J. P. Grandin (Universite de Caen, France) reported experimental results on the effect of strong magnetic fields on autoionizing states.

The second day of the workshop was devoted to applications, dielectronic recombination and concluding remarks by the participants. R. C. Isler (Oak Ridge National Laboratory) and R. Hulse (Princeton Plasma Physics Laboratory) stressed the importance of laboratory measurements of cross sections and theoretical calculations to the modeling of fusion plasmas. W. D. Watson (University of Illinois) reported on the importance of high Rydberg states and dielectronic recombination in providing an interpretation of spectral lines observed in the radio frequency range from interstellar gas and also gave several other examples of the relevance of the topics discussed at the workshop to various topics in astrophysics.

The two sessions on dielectronic recombination (experiment and theory) were particularly timely since most of the experimental groups who have performed measurements of the cross sections for this process were represented as well as a majority of the theorists who have provided detailed calculations.

The recent experiments on dielectronic recombination are of two types: coincidence measurements, where the process is labeled by detecting photons and neutrals as the final state products of a crossed electron and ion beam configuration; and merged beam techniques, in which electron and ion beams are made to follow parallel paths in the interaction region and ions of a lower charge state (or neutrals) are detected. Electric fields are present in all of these experiments and the large discrepancies between measured and calculated cross section are at present attributed to the presence of these fields. Current experimental efforts are aimed at exploring the field effects in more detail.

A summary of recent work on coincidence measurements for magnesium and calcium was given by G. H. Dunn (Joint Institute for Laboratory Astrophysics) and details of a proposed new crossed beam experiment were discussed by J. L. Kohl (Harvard-Smithsonian Center for Astrophysics). Merged beam experiments on carbon were reviewed by J. B. A. Mitchell (University of Western Ontario) and work on lithium and sodium isoelectronic sequence ions was presented by P. F. Dittner (Oak Ridge National Laboratory). J. A. Tanis (Western Michigan University) presented the results of recent measurements on the closely related process of resonant transfer and excitation in atom-ion collisions.

The theoretical session focused on recent attempts to include electric field effects in calculations of dielectronic recombination. V. L. Jacobs (Naval Research Laboratory) gave a summary of the basic theoretical model which is currently being used for this purpose. Recent calculations as well as summaries of the basic theory were presented by Y. Hahn (University of Connecticut) and by D. C. Griffin (Rollins College, FL). The final talk of the session was by J. Dubau (Observatoire de Paris) who discussed the use of dielectronic recombination calculations in modeling dilute high temperature plasmas. This was of special interest since the agreement of these calculations with the results obtained from solar spectra is an important test of the basic theory of dielectronic recombination which complements the recent measurements.

The workshop closed with summary remarks by U. Fano (University of Chicago), A. L. Merts (Los Alamos National Laboratory) and K. T. Lu (Academia Sinica, Beijing, China), and a discussion of future directions led by remarks from the chairpersons of the various sessions. Some of the key observations of the summary session were the following:

1. Our basic understanding of the theory of the Stark effect on Rydberg atoms has advanced to a stage where many of the new experimental results reported could be understood and detailed calculations made to compare with the experimental results. The same is not true for the Zeeman effect or for cases where crossed fields are applied.
2. The effects of electric fields on dielectronic recombination is currently a topic of great interest and the various experiments have not reached a stage where definitve statements could be made as to the adequacy of our current theoretical understanding. Coupled with this was uncertainty of the applicability of calculations with time-independent fields to real plasma-like environments where the fields fluctuate.
3. Exciting new possibilities exist for studies of Rydberg atoms prepared in specific orientations by application of electric and magnetic fields and by controlling their orientation via various experimental techniques.

The above remarks represent only a brief synopsis of the interesting ideas that emerged from the workshop. Those who wish more information should consult the conference proceedings, which has been published as *Atomic Excitation and Recombination in External Fields*, ed. M. H. Nayfeh and C. W. Clark (Gordon and Breach, New York, 1985).

Prepared by *John W. Cooper of the Length and Mass Division of NBS' Center for Basic Standards, and by Charles W. Clark of the Radiation Physics Division in the Bureau's Center for Radiation Research.*

conference report

INTERNATIONAL ASSEMBLY DISCUSSES MECHANISMS OF DNA DAMAGE, REPAIR

For five days, 60 invited speakers, 115 contributors and more than 200 additional attendees probed the mysteries of DNA at the International Conference on "Mechanisms of DNA Damage and Repair: Implications for Carcinogenesis and Risk Assessment," held at NBS.

Donald R. Johnson, director of NBS' National Measurement Laboratory and the chairman of the organizing committee,[1] opened the June 2–7 conference and introduced Ernest Ambler, director of NBS, who greeted the distinguished gathering of foremost experts in the field. The conference chairman, Michael G. Simic, raised the question: "How do we protect ourselves from natural and man-created hazards which damage DNA, and to which we are exposed on a daily basis?"

Meeting for the first time to exchange ideas and perceptions of future trends were scientists dealing with topics as diverse as DNA and protein damage, DNA repair enzymes, the consequences of unrepaired DNA or faulty repair of DNA, site-specific DNA binding drugs, dosimetry of exposure to genotoxic agents, DNA damage in risk assessment, and the role of science in regulatory decisions.

The conference was subdivided into an introduction, three scientific sections, and a poster exhibition. The three sections "Mechanisms of DNA Damage," "DNA Repair and Consequences," and "Risk Assessment" were chaired by distinguished veterans in those fields: George Scholes, Larry Grossman, and Arthur D. Upton, respectively. Each section was further subdivided into half-day sessions. In all of the sessions the primary objective was to discuss the mechanisms of phenomena at the molecular level.

As was pointed out repeatedly, we are exposed to many actual and potential hazards. It is now becoming increasingly clear that we cannot devote all our resources to the investigation of hazardous aspects of all agents to which we are or might be exposed. Consequently, mechanistic understanding of deleterious processes is becoming necessary to assure predictability with high degree of certainty. Hazardous agents can have numerous consequences. The conference dealt predominantly with one of these consequences—cancer, and the role of DNA in carcinogenesis.

The mechanisms of carcinogenesis are not clear at present, in spite of tremendous advances made in the last decade. However, DNA is recognized as one of the major participants in at least one step of what has been recognized as a multistep process. This multiplicity of steps makes the study of the mechanisms of carcinogenesis extremely complex. It also renders prediction of the carcinogenicity of agents unreliable, particularly for weak carcinogens. From the point of view of safety, should we pay more attention to initiators or to promoters?

Conclusions based on available statistics and accidental human exposure are inadequate because comprehensive information is rarely available and accidents are statistically small in size. This has prompted extensive use of animal studies. Unfortunately, direct extrapolation from animal models to humans is, in many cases, difficult. For example, in a well publicized case, BHT has been demonstrated to be carcinogenic in rats only.

The other major issue in carcinogenesis is the acceptable level of exposure. Can one extrapolate the carcinogenic effect down to low levels of exposure, or is there a "threshold" below which the exposure does not cause cancer?

Similar questions were raised by Dr. Ambler in his opening remarks. He pointed out the widespread use of ionizing radiations in medicine and technology. He reminded the audience of the prospective exposure to radiations in space of personnel associated with gravitationless technologies. He also raised concern about the danger of radon as a potential carcinogen. The carcinogenic nature of radon is indicated by statistical studies, and the presence of this insidious gas in our homes is of considerable concern. He pointed out the long tradition of NBS in the measurements of ionizing radiations, and the necessity to develop new measuring approaches, through mechanistic studies of DNA damage and repair, for an accurate assessment of the exposure levels of humans to ionizing radiations. These studies would assist us not only in critically evaluating the extrapolation

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[1] Also made up of C. Reimann, S. A. Miller, D. Longfellow, E. Clementi, M. Kasha, P. Cerutti, G. Scholes, J. M. Brown, and E. L. Powers.

of the effects of low radiation dose levels, but also in manipulating those effects in our favor by preventive measures and treatments.

In his keynote address, Rep. Don Ritter of Pennsylvania talked about the hazards of an advanced technological society. He indicated that risk assessment is one of the critical aspects of hazards control that our society cannot ignore. He appealed to the scientists to work towards a sound scientific basis for risk assessment. Risk must be quantified by accurate measurements (e.g., risk assessment dosimetry). For fiscal reasons we shall never be able to protect ourselves from all potential hazards. Choices based on reliable scientific predictions must be made so that we can protect ourselves preferentially from the most hazardous exposures, he said.

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The importance of science in risk assessment and the associated measurements of exposure to hazardous materials was also emphasized in the introductory presentation of David P. Rall, director of the National Institute of Environmental Health Sciences at Research Triangle, NC. He also mentioned the extensive activities in these areas that are being conducted at his institution.

The final opening remarks were given by Richard H. Adamson, director of Cancer Etiology at the National Cancer Institute in Bethesda, MD. He emphasized the very latest development in carcinogenesis—oncogene research. Understanding the mechanisms of oncogene activation may become the key to prevention and treatment of cancer.

Session I dealt with the mechanisms of free radical reactions in model systems. Free radicals have been implicated in chemical carcinogenesis. However, related free radical reactions have not been identified. Free radicals generated by ionizing radiations are responsible for DNA damage and its consequences. The significance of different radicals in inactivation of ϕX174 DNA was discussed by J. Blok. New kinetic and mechanistic information regarding DNA base damage, strand breaks, and crosslinking was presented (M. G. Simic). The yield of DNA strand breaks was shown to be dependent on fast chemical repair by intracellular thiols (B. D. Michael). Direct ionization of bases by lasers can also result in strand breaks (D. Schulte-Frohlinde). The photoionization approach allows kinetic and mechanistic treatment of damage induced by the direct action of radiation. Photoionization and chemically induced ionization (oxidation) (Jovanovic and Simic) are novel approaches in the study of direct effects, yet are of primary importance in understanding the biological effects of ionizing radiations.

Direct free radical detection by ESR was presented by M. Symons and discussed by J. Herak. Analysis of radiolytic products was elaborated by J. Cadet. Inactivation of enzymes by free radicals was touched upon by R. L. Willson. It may be concluded from this session that time-resolved techniques, such as pulse-radiolysis and laser photolysis, coupled with product analysis, will play an important role in the study of free radical processes in biology and medicine in the next decade.

Sessions III and IV (the Session II discussion is reported later in this account) dealt with mechanisms of DNA damage in cells by various drugs, chemicals, ionizing radiation, and autoxidation processes. Crosslinking within DNA, between DNA and proteins, and various approaches to measure crosslinks showed signs of renewed interest (K. Kohn). Renewed interest in light- and radiation-induced crosslinks was evident from the special poster session (A. Cress, L. Mee, and S. J. Adelstein; M. G. Simic and M. Dizdaroglu; M. J. Peak and J. G. Peak) which was reviewed by N. L. Oleinick. However, the biological consequences of crosslinking are not yet fully understood, except for the crosslinks generated by light-induced cyclobutane dimer formation (thymine dimer, psoralin, etc., in Session V). D. B. Ludlum presented mechanisms of DNA modification and repair induced by mutagenic sulfur mustards and nitrosourea. The sequence specificity of anthramycins and other compounds that bind covalently in the minor groove was explored by L. H. Hurley, using defined DNA sequences, the techniques of "footprinting," and Maxam-Gilbert sequencing. Carcinogens of various kinds also show selectivity in their action, reflecting the base composition, nucleotide sequence or conformation of DNA, the structure of chromatin, or transcriptional activity of different genes (G. N. Wogan).

Other agents, often described as tumor promoters, cause a similar (prooxidant) state, and it may be that the prooxidant state itself serves to promote tumorigenesis...

One effect of radiation is to produce a prooxidant state in cells. Other agents, often described as tumor promoters, cause a similar state, and it may be that the prooxidant state itself serves to promote tumorigenesis, after initiation has ocurred (P. A. Cerutti). The mechanisms may require modulation of regulatory genes, mediated perhaps by poly ADP ribosylation which is itself sensitive to the prooxidant state.

In Session IV, (mainly about the effects of ionizing radiations), J. F. Ward indicated the nonhomogeneity of damage and discussed some of its consequences. For example, he demonstrated that it is impossible to distinguish true double strand breaks which involve base destruction on both strands and loss of genetic information from single strand breaks on the two strands offset by a few bases (which are, in principle, repairable without loss of information). On a related topic, P. E. Bryant showed that some double strand breaks arise from the action of repair enzymes on base damage opposite a single strand break. He described a model system for double strand breaks in which these are created intracellularly by the action of restriction endonucleases. J. Lett has studied the eventual appearance of DNA damage in nondividing rabbit retina cells years after irradiation and apparent recovery of the DNA from the immediate effects of radiation. R. E. Meyn described differences in the yield of ionizing radiation damage in different tissues in vivo (perhaps reflecting relative levels of hypoxia), and also varying capacity to repair damage.

Strand breaks created by enzymic incision are present only transiently after UV damage (K. Erixon). DNA synthesis inhibitors cause incomplete repair sites to accumulate, leading to high levels of breaks. M. Chevion showed that double strand breaks can be induced by Fe and Cu ions, hydrogen peroxide, and physiological reductants, mimicking the multiple damage sites induced by radiation.

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Section 2, subdivided into Sessions V–VII, dealt with the mechanisms of enzymatic repair of damaged DNA. (Chemical repair of damaged DNA at the free radical stage was not part of the conference program since it was already discussed at the conference on "Radioprotectors and Anticarcinogens," held at and sponsored by NBS in 1982.)

In the first session on the repair of DNA damage, D. Mount reviewed the regulation of excision repair and SOS repair in *E. coli*. He described a *lex A* mutant that produces an unstable repressor of repair genes, leading to increased expression of *uvr A, B,* and *D*. Excision is consequently elevated in these cells. The *uvr A, B, C* genes have been cloned (L. Grossman), and used to produce large quantities of protein products. Excision repair activity was tested *in vitro*, utilizing a pyrimidine dimer in a specified sequence. Cuts are made on each side of the dimer, but the oligonucleotide is released only when helicase II (*uvr D* gene product) and DNA polymerase I are present with dNTPs.

The repair of dimers by *M. luteus* UV endonuclease entails a two-step incision (R. H. Grafstrom). The N-glycosylic bond of the 5′ pyrimidine of the dimer is broken, leaving the dimer attached to the backbone via the 3′ base; the resulting apyrimidinic site is then cleared by an endonuclease activity. *M. luteus* and T4 endonucleases are similar. The gene coding for the latter, *den V*, has been cloned and introduced into *E. coli*, yeast, and the UV sensitive CHO mutant UV-5 (J. K. de Riel). In all organisms studied, excision repair was partially or completely restored.

E. C. Friedberg described the *RAD* genes of yeast. Five have been cloned, and all found necessary for the incision of DNA after UV induced damage. Four have been completely sequenced, and mutation at specific sites has defined regions essential for repair. Two genes have been mapped on particular chromosomes. *RAD* genes do not complement *uvr A, B, C, D* mutations in *E. coli*.

Two repair activities were featured in T. Lindahl's talk—a glycosylase, which acts on various altered forms of thymine, and the methyl-transferase or Ada protein from *E. coli*. This protein has two acceptor sites for methyl groups, with one accepting from 0^6-methylguanine, and the other from phosphotriesters. It is possible that the second reaction is involved in autoregulation, activating the *ada* gene and inducing an adaptive response.

Some repair enzymes that appear to be effective against low doses of damaging agents can be overwhelmed at high doses because the enzymes cannot be replaced by cells fast enough. Therefore, if the enzymatic system functions properly, cancer will not result from low, chronic doses of certain kinds of carcinogens.

Metabolic alterations of DNA were discussed by B. Weiss. The presence of thymine, rather than uracil, in DNA may reflect the common occurrence of spontaneous deamination of cytosine in DNA, creating uracil. If uracil were a standard constituent of DNA, a repair mechanism would have to distinguish "accidental" from "intended" uracils. Mutants of *E. coli* lacking dUTPase are unable to make dTTP, and have been used to examine the effects of replacing thymine with uracil in the DNA.

The *umuDC* operon in *E. coli* is involved in mutagenesis (L. Marsh). It, and its plasmid analogue, *mucAB*, have been cloned and sequenced. A model for its action proposes that during replication, polymerase III becomes blocked at the site of damage, but that it can interact with *umuD C* and *recA* products. This allows polymerization to continue with the risk of introducing alterations at the site of damage.

Apurinic (AP) sites are common intermediates in mutagenesis (L. A. Loeb). In a phage reversion assay, it was found that the predominant DNA sequence alteration was the substitution of deoxyadenosine opposite the AP site. Possible AP sites are common intermediates in mutagenesis: replication may stop at a bulky adduct until the adduct is removed, leaving an AP site, at which point the polymerase resumes synthesis, and an adenine is introduced.

Mistakes in normal replication—mismatches—are likely to lead to mutation unless the repair process can discriminate newly synthesized from parental strands. Discrimination might be on the basis of methylation (new strands being unmethylated), and P. Modrich confirmed that in *E. coli* mismatch correction occurs on the unmethylated strand. In his model, a methyl group acts as a reference point for the repair system. Mismatches do not occur only through faulty replication. Common mistakes might result, for example, from the conversion of methylated cytosine to thymine rather than cytosine, giving a GT base pair; these are efficiently recognized and restored to the correct form in an *E. coli* assay system using defined heteroduplex DNA molecules (M. Radman). The cell may be programmed to recognize such mispairings and to make the correction on the right strand. Mismatch repair occurring on both strands may account for double strand breaks. In higher organisms, recombination repair of double strand breaks may be the origin of sister chromatid exchange.

In higher organisms, recombination repair of double strand breaks may be the origin of sister chromatid exchange.

F. Hutchinson reviewed the classification of mutations. Targeted mutations depend on a lesion in the particular gene to initiate the mutational event; nontargeted mutations can occur in undamaged DNA, and result from an infidelity of replication. Different agents produce different spectra of mutations—transitions (e.g., GT), transversions (e.g., AG), frameshifts, large deletions/insertions, and double events. Spontaneous mutations in the *lac I* gene of *E. coli* have been examined for evidence of sequence specificity (B. W. Glickman). There is a frameshift hotspot in the region of tandemly repeated tetramer. Deletions tend to occur where repeated sequences lend stability to a misalignment. Single base frameshifts may result from DNA repair.

Bridging the gap between prokaryotic and eukaryotic organisms, M. Seidman described the use of shuttle vector plasmids, able to replicate in both bacteria and mammalian cells. Plasmids treated with DNA-damaging agent are introduced into mammalian cells, where replication, repair, and mutation occur. A marker gene on the plasmids allows monitoring of these processes by assaying the appropriate activity (coded by the marker gene) in a bacterial host. Mutations introduced in the plasmid can be characterized in terms of sequence changes. The novel plasmid described by Seidman has a low rate of spontaneous mutation. K. H. Kraemer used an expression vector plasmid, containing the gene for chloramphenicol acetyltransferase. Pretreatment of plasmid with UV before introducing it into human cells caused a decrease in CAT activity, with the extent of the decrease reflecting the DNA repair phenotype of the cells. Thus, UV inactivation of CAT expression was greatest in XP cells.

L. D. Samson described an adaptive response to alkylating agents in certain mammalian cell lines. Pretreatment with a low level of alkylating agent renders cells resistant to a subsequent acute, high dose. She ascribed this important effect to an increase in 0^6-methylguanine transferase activity. An antibody has been produced to the *E. coli* methyltransferase, and this has been used to identify putative human methyltransferase.

A general response to severe DNA damage is the stimulation of poly(ADP-ribose) synthesis, with consequent reduction in NAD and ATP concentrations in the cell. N. A. Berger suggested that the disruption of energy-dependent processes such as RNA, DNA, and protein synthesis might serve as a suicide response, killing the cells to protect the organism from possible mutational effects.

H. Zarbl and M. Barbacid described investigations into the role of *ras* oncogenes in carcinogenesis—in particular, the question of whether oncogene activation is an effect, rather than a cause, of carcinogenesis. In tumors induced by a single treatment with a chemical carcinogen, transforming H-*ras* oncogene is very common, and the activation (i.e., base alteration) is at a particular point in the DNA sequence. The type of change is specifically related to the carcinogen used, which suggests that the activation is a direct result of carcinogen damage rather than a secondary effect of carcinogen-induced transformation. Another oncogen c-*myc*, becomes activated not by a point mutation, but rather by translocation, proviral integration, or amplification, giving high levels of *c-myc* expression (M. D. Cole). Interestingly, interferon can cause reversion of the transformed phenotype, and the oncogene is then no longer expressed. When the transformed cell was mer^- (i.e., unable to repair O^6-methylguanine), the nontransformed revertants produced with interferon treatment had restored methyltransferase activity and were resistant to alkylating agents (R. S. Day). Thus, there appears to be a close link between oncogene activation and the mer^- phenotype. M. Barbacid indicated that G→A change by NMU can activate an oncogene in a much earlier stage of multistep cancer development than previously believed.

An important assessment of the current activities in the study of mutagenic changes on DNA, and a novel approach to these studies, was suggested by M. Radman. Complete sequencing of DNA is an enormous task that cannot be achieved by present techniques. Rather than investing enormous resources into it, he suggested development of methodologies which would decode the sequence differences only.

The question of what to do about faulty repair and the sequences which may lead to cancer was addressed in Session II dealing with DNA binding agents. In his introductory remarks, J. W. Lown indicated the potential importance of site specific DNA binding drugs in cancer treatment. J. B. LePecq described novel molecules whose remarkably high affinity for DNA derives from a dimeric or trimeric arrangement of intercalating moieties. Neocarzinostatin binds to DNA by intercalation and causes DNA damage—strand breaks, release of free base, and covalent adducts of both alkalilabile and highly stable forms (I. H. Goldberg). Computer modeling allows the study of possible interactions between side-chains of intercalators and particular DNA sequences in designing new anti-tumor drugs (S. Neidle). The anti-tumor drug netropsin does not intercalate with DNA, but rather binds in the minor groove of the helix. The specificity and geometry of this binding have been the subject of studies by x-ray crystallography (R. E. Dickerson).

Computer modeling allows the study of possible interactions between side-chains of intercalators and particular DNA sequences in designing new anti-tumor drugs.

If specific sequences could be identified in oncogenes or in the DNA of cancer cells, then site-specific drugs could be designed either to prevent development of cancer or to kill cancerous cells. This elegant approach could become an important solution in our continuing fight against carcinogenesis.

Section 3 on Risk Assessment was introduced by Sanford A. Miller, director of the center for Safety and Applied Nutrition of the FDA and a member of the conference organizing committee. He pointed out the difficulties associated with safety assessment of foods and the highly responsible role of FDA in ensuring the safety of our food supply. One should not forget, of course, that classical processing of foods or even natural foods can be detrimental (see, e.g., Dietary Carcinogens and Anticarcinogens, by B. Ames, *Science*, **221**, 1256, 1983).

Session VIII dealt with the measurement of exposure to genotoxic compounds. Classical aromatic adducts to DNA were discussed by F. Kadlubar, and W. G. Thilly talked about how to discriminate different patterns of genetic change induced by different mutagens. Steve R. Tannenbaum, the chairman of the session, presented the use of blood proteins as alkylation dosimeters in general exposure dosimetry. H. Bartsch talked about population studies in areas of Japan, China, and India having little population migration, and in which urine tests were used to determine levels of endogenous formation of N-nitroso compounds and to learn how these levels are affected by dietary components and modifying chemicals.

J. D. Groopman presented the use of monoclonal antibodies for detection of carcinogens and their adducts, which are produced by molds in foods, fuel combustion, and cigarette smoking. S. S. Wallace and R. A. Floyd told of novel approaches in the measurement of thymine glycol and 8-hydroxyguanine, which are two major products of DNA base damage.

The Scientific Basis for Genotoxic Risk Assessment, Session IX, was chaired by P. N. Magee. P. C. Hanawalt described repair of DNA as a selective process. Cells of xeroderma pigmentosum show a low level of UV excision repair, but this response is heterogeneous. Certain DNA domains are repaired at normal rates, while the rest of the DNA shows deficient repair. The repetitive α DNA in African Green Monkey cells is repaired very poorly after certain kinds of damage. Most recently, it has been found that an actively transcribing gene in CHO cells is repaired at a much higher rate than other genes. Understanding these novel fine points of DNA repair and how cells prioritize the repair of "housekeeping genes" is vital to the interpretation of DNA damage in risk assessment. R. M. Santella and R. Perera discussed the use of monoclonal antibodies for quantitation of damage to both DNA and blood cells, and implications of these measurements to risk assessment. R. L. Saul and B. N. Ames presented data on the background levels of DNA damage in the population obtained by measuring thymine glycol in urine. R. H. Reitz discussed the role of pharmacokinetics in risk assessment, and R. Parshad talked about G_2 chromosal radiosensitivity, which he associated with deficient DNA repair and cancer susceptibility.

Session X, Risk Assessment and Regulatory Decisions, was chaired by A. D. Upton. Comments on mechanistic considerations were given by Upton. Use of models in low-dose extrapolation (J. Van Ryzin), problems in interspecies extrapolation (R. Wilson), and the time-to-tumor approach in risk assessment and risk management (R. E. Albert) indicated that mechanisms of DNA damage and repair have not become an integral part in current risk assessment considerations. It was also clear that novel scientific approaches in assessing thresholds and risk are badly needed.

Session XI, the last session, dealt with risk assessment of foods, an overview on which was given by W. G. Flamm, session chairman. The role of risk assessment in food safety policy was discussed by R. J. Scheuplein; mutagens and carcinogens in food, by M. J. Prival; and practical aspects of risk assessment of foods, by R. J. Lorentzen. An important role of foods relative to DNA damage was presented by Carmia Borek. She discussed the significance of nutritional factors in cellular protection against DNA damage.

The program of the conference was principally oriented towards relationships between the mechanisms of DNA damage and cancer, with cancer prevention in mind. However, there are many other diseases, and aging in particular, in which approaches similar to those reviewed for cancer should be pursued.

> ***However, there are many other diseases, and aging in particular, in which approaches similar to those reviewed for cancer should be pursued.***

The motto of the conference was "DNA is the beginning and the end." Any effort that can postpone "the end" and improve the quality of life in the interim by preserving or manipulating the integrity of DNA is worth our unselfish commitment and highest priority.

> ***DNA is the beginning and the end.***

The proceedings of the conference will be published in a didactic form by Plenum Press in 1986.

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MICROBES PLAY A CONSIDERABLE ROLE IN CORROSION

Reports from industrial, academic, and government laboratories provided an International Conference on Microbiologically Induced Corrosion with persuasive evidence that microorganisms are of considerable importance in establishing corrosion on a wide variety of structures in a number of industries. Held at NBS, the conference was co-sponsored by the Research Committee, National Association of Corrosion Engineers, and NBS under the chairmanship of Dr. Stephen C. Dexter of the University of Delaware at Lewes. It was the second of its kind to be held internationally, the first being held at the National Physical Laboratory, Teddington, England in March 1983.

Approximately 125 persons, representing 13 countries and 26 of the 50 states in the U.S., attended the three day conference. Thirty-nine papers on microbial corrosion were presented. They dealt with historical perspectives and current problems, case histories, mechanisms, experimental methods, and control procedures.

In his welcoming address, Raymond Kammer, of NBS, said a good portion of the cost of corrosion in the United States, estimated to be $167 billion in 1985, was biologically induced. He spoke of the long history of NBS involvement in underground corrosion, a significant portion of which is probably biologicaly induced.

HISTORICAL PERSPECTIVES AND CURRENT PROBLEMS

R. Starky, formerly of Rutgers University, New Brunswick, NJ, and for many years the foremost investigator in the U.S. on biological corrosion (primarily anearobic corrosion caused by sulfate-reducing bacteria (SRB)) examined the contributing corrosion factors, including sulfide and iron-sulfide. He stated the need for a critical reexamination of all of these factors which contribute to anaerobic corrosion.

The European research investigations directed toward an understanding of the mechanisms of microbial corrosion were summarized by K. Tiller of the National Corrosion Service, National Physical Laboratory, Teddington, England. Tiller, who for many years has headed the foremost biological corrosion research group outside the U.S., also discussed the advances made in assessing the corrosivity of a wide range of environments as well as some of the problems in the offshore oil and gas industry.

A recently published literature review on microbiologically influenced corrosion (MIC) was prepared for the Materials Technology Institute of the chemical process industries in cooperation with an interdisciplinary group of scientists at Rensselaer Polytechnic Institute. D. Pope summarized the conclusions of this review, which included current corrosion problems in the chemical process industries and recommendations made by the group regarding research priorities.

CASE HISTORIES

Reports of MIC in a number of processes and industries as well as of various ferrous and nonferrous alloys were presented. In many cases, SRB were associated with the corrosion process. An unusual case of welded mild steel and 304 stainless corrosion by blue-green and red algae, however, was described by C. R. Das, Ravenshaw College, Cuttack, India. C. R. Schmitt, Bechtel National Inc., Oak Ridge, TN reported on a case which he believed to be due to microbiological pitting of an aluminum heat exchanger exposed to potable water.

Cases of MIC found to be associated with SRB included those in oil production systems, reported by P. F. Sanders, University of Aberdeen, Scotland; cooling water systems in alcohol distillation plants, reported by J. O. Silva, Aquatec Commercial Ltda, Sao Paulo, Brazil; the power industry, reported by M. Bibb, ESCOM, Johannesburg, South Africa; and cathodically protected offshore structures, reported by G. Eidsa, Central Institute for Industrial Research, Oslo, Norway.

MIC of mechanically superior spun ductile iron pipe, used to replace spun grey iron pipe in the U.K. water industry in the 1960's as a result of SRB activity, was investigated by R. A. King and co-workers, University of Manchester Institute of Science and Technology, Manchester, England. King reported that the biological processes were similar on both materials; the corrosion performance of the new spun ductile iron pipes not being as good as was expected. R. Patenaude, of the Wisconsin Division of Highways, Madison, reported that field observations and tests indicated that nearly one-half of the corrosion of steel culvert pipe in Wisconsin was related to the activity of SRB. Perforation of underground brass pipes of low zinc content (91.6% Cu; 8.22% Zn) in less than two years of use was explained by N. De Cristofaro, Instituto Nacional de Technologia Industrial, San Martin, Argentina, as being due to the metabolic products of SRB.

MECHANISMS

MIC has been attributed to one or several of the following mechanisms: 1) removal of hydrogen (electrons) from the surface of a metal (cathodic depolarization) through the activities of the bacterial enzyme, hydrogenase; 2) creation of oxygen or chemical concentration cells; 3) formation of corrosive metabolic products; 4) destruction of passive or protective films; and 5) inactivation or destruction of microbiological or corrosion inhibitors.

The session on mechanisms was introduced by R. E. Ricker, University of Notre Dame, South Bend, IN, who described the possible and probable electrochemical mechanisms by which microorganisms initiate or enhance corrosion reactions. Special emphasis was devoted to the concepts of "depolarization" and "depassivation."

Enhanced production of hydrogenase, the enzyme critical to the cathodic depolarization mechanisms, by SRB in the presence of high surface clays, silicas, and several modified silicas, was reported by R. E. Williams, National Research Council, Ottawa, Canada.

F. A. Tomei, Harvard University, Cambridge, MA, employed a non-electrochemical technique to demonstrate the cathodic depolarization effect by the SRB hydrogenase system. Fumarate, instead of sulfate, was utilized as an electron acceptor, being reduced to succinate, the appearance of which could be measured. Thus the formation of succinate or the disappearance of furmarate could be used as an indirect measure of hydrogen uptake from the metal surface and thereby a measurement of the corrosion rate could be afforded. The highest corrosion rate determined, using this system was 33 milligrams per square decimeter per day, but this was still lower than the corrosion rates observed in the field.

Several papers were concerned with formation of concentration cells by mixed populations of bacteria or consortia, appearing as biofilms on metal surfaces, which create oxygen depeleted conditions for the development of SRB. W. A. Hamilton, University of Aberdeen, Scotland reported on the development of a (^{35}S) radiorespirometric method to determine the activity of SRB within the biofilm on metal test coupons. Results obtained by this technique are compared with the amount of marine fouling and corrosion occurring. The technique would appear to have considerable value for monitoring corrosion in the field and evaluating the efficacy of corrosion-protection methods. The use of this technique within the ballast legs of large concrete oil production platforms in the north sea off Scotland was described by S. Maxwell, Corrosion Specialists (North Sea) Ltd., Aberdeen, Scotland. The rate of sulphate reduction on mild steel coupons exposed in the entrained seawater was found to be very high on the metal's surface but below detection in bulk phase samples.

The formation and ecology of surface colonization on metals which may result in corrosion was graphically illustrated by J. W. Costerton, University of Calgary, Canada. Within complex microbial consortia, local differences in protons and other cations, substantially different from those of the general biofilm, are produced, which Costerton stated, form local electrochemical corrosion cells. SRB are found in most of these cells, but need not be, to induce corrosion.

D. C. White, Florida State University at Tallahassee, outlined the physical (Fourier transform infrared spectroscopy) and chemical methods which he used to analyse surface biofilms on the surface of metals on a scale approaching the size of microcolonies of bacteria. He reported his findings on the accelerated corrosion of 304 stainless steel in seawater by an aerobic marine pseudomonad and its polysaccharide exopolymer, as well as by two Vibrio species with exopolymers of unknown composition.

Studies on the comparison of abiotic vs. biotic oxygen concentration cells in MIC were presented by B. Little, Naval Oceanographic Research and Development Agency, Mississippi and S. Dexter, University of Delaware at Lewes. Studies, using nickel 201 and thermophilic bacteria, according to Little, indicated that the bacteria did not increase the corrosion current over abiotic oxygen concentration (differential aeration) cells in the presence of the acidic metabolites, isovaleric and isobutyric acids. Dexter, in a study of crevice corrosion initiation, found that oxygen was depleted within a 304 stainless steel cell, containing sterile sea water, much more effectively (150:1) than in a nonmetallic (teflon) nonsterile cell with natural seawater.

Two studies on metal deterioration by metabolic products were reported. In a study of hydrogen producing bacteria, M. Walch, Harvard University, Cambridge, MA, reported that small amounts of hydrogen were absorbed by metals beneath films of these bacteria. Hydrogen uptake by some metals can initiate hydrogen embrittlement of these metals. W. Iverson, NBS, indicated that some SRB produce a volatile, phosphorus compound which is highly corrosive to mild steel. This compound can also be produced by the action of hydrogen sulfide on certain phosphorus compounds. Anaerobic corrosion may be initiated when a film of iron sulfide, produced by SRB generated hydrogen sulfide, breaks down and permits the phosphorus compound to come in contact with the steel surface. Iverson suggested that the breakdown of this iron sulfide film may be detected by an electrochemical noise technique.

Destruction of passive or protective films, the fourth mechanism previously mentioned, was the subject of two papers, one by D. W. S. Westlake, University of Alberta, Edmonton, Canada and the other by H. Videla, INIFTA, La Plata, Argentina. Westlake reported on the corrosive effect of certain pseudomonas species on the interior of oil pipelines in Alberta which have the capacity to reduce ferric iron to ferrous iron, as well as the ability to reduce sulfite, thiosulfate and sulfur (but not sulfate) to sulfide. The corrosive effect, he stated, was due to the ability of these organisms to remove or prevent the formation of a protective film of ferric iron by reducing this insoluble film to soluble ferrous iron. Videla described his work on the electrochemical behavior of prepassivated SAE 1020 steel in the presence of SRB. He stated that the corrosion process was initiated by the replacement of the passive film on the steel by a poorly protective film or iron sulfide (mackinawite), which was followed by pitting at these sites.

Combination of the described mechanisms undoubtedly play a part in many corrosion processes. Such a role was described by Videla in another study on the corrosion of aluminum by the fungus *Cladosporium resinae*, using electrochemical techniques (potentiostatic) together with SEM-EDAX analysis. From these studies, he concluded that the localized corrosion of metal was due to: 1) a local increase in the hydrogen ion concentration due to organic acid production; 2) a decrease in the stability of the passive film by metabolic substances; and 3) a decrease in the concentration of corrosion inhibitors due to their utilization by the organisms.

EXPERIMENTAL METHODS

R. Tatnall, E. I. duPont de Nemours & Co., Wilmington, DE, introduced the session on experimental methods by outlining a general, recommended program to study MIC. He stated that many methods used in other fields are not applicable to biocorrosion phenomena.

A more accurate simulation of environmental conditions for microbiological corrosion testing was stressed by R. G. J. Edyvean, University of Sheffield, England. He stated that two methods, artifical seawater or a sodium chloride solution saturated with hydrogen sulfide, are used to test steels (for offshore use) for corrosion fatigue cracking. The hydrogen sulfide concentration in saturated seawater (3150 ppm) is far more aggressive than typical concentrations found under marine fouling conditions (~ 100 ppm). New experimental methods were described.

The use of mixed cultures of bacteria, which more accurately reflect environmental conditions, in studying anaerobic corrosion, was reported by C. Gaylarde, City of London Polytechnic, England. Testing the effect of three bacterial cultures, including one SRB, on the corrosion of mild steel coupons singly and in combination, various inhibitory and enhancement effects were noted.

F. Kajiyama, Tokyo Gas Company, Japan, reported on his successful laboratory attempt to simulate the high rate of corrosion of ductile iron in anaerobic soils. High rates of corrosion, 2 millimeters per year were reproduced by establishing a test cell between two soils with different SRB activities (cell numbers). Both anode and cathode were of the same material, the anode being of smaller surface area than the cathode (ratio:1 to 1000). The SRB activity in the vicinity of the anode, according to Kajiyama, played a vital role in the corrosion process.

AC impedance and electrochemical noise techniques were found useful by A. N. Moosavi, University of Aberdeen, Scotland, in monitoring the corrosion rate and in studying the type of corrosion process in reinforcing steel. The sulfide produced by SRB was found to have an adverse affect on the durability of the bond between the reinforcing steel and concrete.

Several techniques to rapidly detect and identify organisms which may be involved in MIC were described by Pope. These techniques involve indirect labelled antibody techniques. Secondary antibodies coupled to biotin and fluorescently labeled Avidin, permit cells reacting to the primary antibody to be observed, using a fluorescence microscope. A similar technique permits use of the light microscope by coupling the Avidin to an enzyme which with an appropriate substrate produces a colored product. These enzyme-secondary antibody reagents have been used to develop macroscopic color tests with rapid and semi-quantitative estimation of specific organism which may be present in the corrosion products.

CONTROL PROCEDURES

The University of Manchester's King described various measures to control microbial corrosion, external and internal, in long, large capacity, subsea pipelines. These include bacterial monitoring, biocide treatment, and cathodic protection by sacrifical anodes.

A routine procedure for external corrosion protection of pipelines has been to apply cathodic protection, polarizing the pipe to a standard-850 mV with respect to a saturated $Cu/CuSO_4$. In areas where there is a lot of activity due to SRB, this potential is not sufficient. Potentials of −950 mV have been recommended. R. G. Worthingham, NOVA/Husky Research Corporation Ltd., Calgary, Canada, stated that bacterial corrosion occurred beneath disbonded plastic tape coatings even when the cathodic protection potentials were well above −1000 mV. Laboratory studies by NOVA to determine the cathodic protection criteria to control anaerobic bacterial corrosion were described by T. R. Jack, also of NOVA/Husky.

An overview of MIC in industry was presented by J. G. Stoecker, Monsanto Co., St. Louis, MO. He reviewed the progress made toward understanding this type of corrosion as well as the future needs of corrosion engineering to present or minimize the potential of MIC still further.

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