Determination of Aluminum in Precipitation Hardening Stainless Steel and High Temperature Alloys

Lawrence A. Machlan, John L. Hague, and Edward J. Meros

A procedure is described for the determination of aluminum in high temperature alloys. Aluminum is selectively precipitated with 8-hydroxyquinoline from an ammoniacal solution of the alloy containing citrate and cyanide as complexing agents. The precipitate is ignited under oxalic acid, the oxides fused, and dissolved in acid. A caustic precipitation is made, an aliquot of the filtrate treated with hydrogen peroxide, and the aluminum precipitated with 8-hydroxyquinoline. The aluminum hydroxyquinolate is filtered on a fritted-glass crucible, dried, and weighed.

1. Introduction

One of the interesting developments in metallurgy during the last few years has been the emergence of high temperature alloys and precipitation hardening stainless steels as an important group of alloys. Many, if not most, contain aluminum as an alloying addition. All contain chromium, and varying amounts of iron, cobalt, and nickel as major constituents. Titanium, zirconium, and molybdenum are frequently present as alloying additions; less frequently, niobium and tungsten may also be used.

This combination of elements makes the determination of aluminum by chemical methods a vexing one. An embarrassingly large number of choices is available when it comes to choosing separative and determinative steps for an analysis, and most can be made to work under proper conditions; in fact, it has been said with some justification that there are almost as many methods for determining aluminum as there are analysts willing to write them. It is beyond the scope of this paper to present a comprehensive survey. The method which follows is a useful combination of steps that has been used over a period of years in the Bureau and found to have better than average reliability.

The sample, usually 2 g, is dissolved in a nitric-hydrochloric acid mixture. Citric acid is added as a complexing agent, and the solution made ammoniacal. Sodium cyanide is added to form complexes with nickel, iron, copper, and cobalt, and the aluminum precipitated by the addition of 8-hydroxyquinoline. The precipitate is filtered, ignited after the addition of oxalic acid, and the ignited residue treated with sulfuric and hydrofluoric acids to eliminate silica. The residue is fused in bisulfate, leached in hydrochloric acid, the solution partially neutralized, and a sodium hydroxide precipitation made. An aliquot of the filtrate (usually representing 1 g of sample) is treated with hydrogen peroxide and sodium cyanide, and the aluminum again precipitated with 8-hydroxyquinoline, filtered, dried, and weighed.

The separation of aluminum with 8-hydroxyquinoline in the presence of cyanide was originally described by Heczko [3] [1] in 1934. In conjunction with a sulfide separation to remove manganese, it has been used for some years as a simple routine procedure for the determination of aluminum in nitriding steels. Unfortunately the method lacks specificity, as zirconium and titanium, to name two elements, are serious interferences. Tartaric acid is usually used [6, 7] to minimize the co-precipitation of chromium, but in our experience citric acid is somewhat better in this respect. From experiments covering a range of concentrations, the amounts of citric acid and sodium cyanide were chosen as about the minimum quantities required to consistently give a reasonably clean separation of aluminum from chromium, nickel, cobalt, and iron.

A discussion of the sodium hydroxide separation is almost redundant. Much pertinent information will be found in an article by Bright and Fowler [1]. The separation serves to remove manganese, titanium, zirconium, and magnesium among others [4], as well as the remainder of the major elements. Since the latter are largely eliminated in the previous step, the precipitation is run under controlled conditions in the presence of a small addition of iron. Stainless steel beakers and polyethylene beakers and funnels can be used, and obviate the use of expensive platinum, or the use of glassware in contact with strongly alkaline solutions.

Hydrogen peroxide is added to the acidified aliquot to complex any residual titanium, niobium, vanadium, molybdenum, etc. The aluminum is precipi-

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tated with 8-hydroxyquinoline, filtered on a glass frit, dried, and weighed. This separation was described by Lundell and Knowles [5] in 1929, and is a convenient method for removing those elements which form peroxide complexes.

The method has proved useful in the determination of aluminum in the 0.5 to 3.0 percent range in a variety of alloys. Experiments on synthetic mixtures indicate the accuracy to be of the order of one percent or better of the amount of aluminum present. The tendency of the final precipitate of the aluminum quinolate to run slightly (about 1%) high almost exactly compensates the small absorption and solubility losses. The method requires more elapsed time than some possible alternatives, due primarily to the steps involving ignition and treatment with sulfuric and hydrofluoric acids. Since these steps do not require much attention, the "working time" is usually about a day for a set of six determinations.

2. Reagents

Citric acid solution (500g/liter). Dissolve 500 g of citric acid monohydrate in 500 ml of diluted sulfuric acid $(1+49)^2$, dilute to 1 liter with water, and filter to remove insoluble material.

8-Hydroxyquinoline solution (75 g/liter of ethanol). Dissolve 75 g of 8-hydroxyquinoline in 900 ml of ethyl alcohol, dilute to 1 liter with ethyl alcohol, and filter.

Cyanide wash-solution. Dissolve 20 g of ammonium chloride, 20 g of ammonium citrate, and 20 g of sodium cyanide in 900 ml of water containing 25 ml of ammonium hydroxide, and dilute to 1 liter with water.

Iron solution (20 mg/ml). Dissolve 10 g of iron containing a negligible quantity of aluminum in 200 ml of diluted hydrochloric acid $(1+3)$, cautiously oxidize with 8 to 10 ml of nitric acid, cool, and dilute to 500 ml with water.

Sodium hydroxide solution (300 g/liter). Transfer 700 ml of water and 300 g of sodium hydroxide to a polyethylene bottle, dilute to 1 liter with water, and mix well.

3. Procedure

Transfer 2 g of the sample to a 600-ml beaker, cover, and add 40 ml of diluted aqua regia $(1+1)$ (3 parts of hydrochloric acid and 1 part of nitric acid diluted with an equal volume of water). Warm the solution on a steam bath until the sample dissolves. Add 40 ml of citric acid solution and adjust the volume of the solution with water to 250 ml. Add ammonium hydroxide until the solution is but slightly acid, add 1 g of hydroxylamine hydrochloride, neutralize to litmus paper with ammonium hydroxide, and add 10 ml in excess. Add 15 g of sodium

cyanide,[3] heat to boiling, and boil 1 to 2 min. Add 25 ml or a sufficient[4] amount of 8-hydroxyquinoline solution slowly while stirring the solution vigorously. Stir the solution vigorously (best done with a mechanical stirrer) for 15 min and allow the solution to stand 15 min on the edge of the steam bath. Add paper pulp, stir the solution well to distribute the pulp, and cool to room temperature.

TABLE 1. *Results of determinations of aluminum by the recommended procedure in various synthetic mixtures*

NBS Standard Sample 169, Ni 77, Cr 20, Al 0.095

Weight of sample	Other element added	Aluminum			
		Added	Present	Found	Difference
g	*mg*	*mg*	*mg*	*mg*	*mg*
2	40 Ti		1.9	1.4	−0.5
2	40 Ti	5.0	6.9	6.5	−.4
2	40 Ti	5.0	6.9	6.7	−.2
2	40 Ti	10.0	11.9	11.7	−.2
2	40 Ti	10.0	11.9	11.8	−.1
2	40 Ti	20.0	21.9	22.2	+.3
2	40 Ti	20.0	21.9	21.7	−.2
2	40 Ti	20.0	21.9	21.9	.0
2		20.0	21.9	21.7	−.2
2	40 Ti	40.0	41.9	42.4	+.5
2	40 Ti	40.0	41.9	42.1	+.2
2	40 Ti	60.0	61.9	62.4	+.5
2	40 Ti	100.0	101.9	101.1	−.8

Filter the solution through a double thickness of close-texture filter paper fitted to a 7-cm Büchner funnel and precoated with a little filter pulp. Transfer the precipitate to the funnel, and wash 5 to 6 times with the cyanide wash solution,[5] and 2 to 3 times with water. Transfer the paper and precipitate to a platinum crucible, cover the precipitate with 5 g of oxalic acid, place the crucible in a cold muffle, and slowly ignite to 600 to 700° C. Add 1 to 2 ml of diluted sulfuric acid $(1+3)$ and 10 to 15 ml of hydrofluoric acid to the crucible, and remove the hydrofluoric and sulfuric acids by heating on an air or sand bath. Add 1 to 2 g of potassium pyrosulfate to the crucible and fuse the salt to dissolve the oxides. Transfer the crucible and fusion to a 400-ml beaker and dissolve the fusion in 100 ml of warm diluted hydrochloric acid $(1+5)$. Remove and wash the crucible with diluted hydrochloric acid $(1+5)$. Add 5 ml of iron solution, nearly neutralize (as indicated by the slow redissolving of the iron precipitate) with sodium hydroxide solution (300 g/liter). Transfer 140 ml of water and 70 ml of sodium hydroxide solution to a weighed[6] 1-liter

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[3] With cyanide present, all operations should be conducted in a hood.
[4] A minimum addition of 25 ml of 8-hydroxyquinoline solution is recommended. In the presence of larger than usual amounts of aluminum or titanium, additional reagent may be required. For example, 40 ml of 8-hydroxyquinoline solution was used in the last experiment given in table 1.
[5] The cyanide wash solution should be handled by air or bulb.
[6] The use of "weight aliquoting" avoids the necessity of washing the precipitate and handling strongly alkaline solutions in contact with glassware. Weighing on a trip balance to the nearest half-gram or so provides adequate accuracy for the present application.

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[2] Diluted sulfuric acid $(1+49)$ denotes 1 volume of concentrated sulfuric acid, sp gr 1.84, diluted with 49 volumes of water. If no dilution is specified, the concentrated analytical reagent is meant.

stainless steel beaker. Heat the sodium hydroxide solution to boiling, add the sample solution slowly with good stirring, and boil for 1 to 2 min. Cool the solution to room temperature, dilute with water to 500 g, stir thoroughly, and allow the precipitate to settle for a few minutes. Filter through a close-texture paper fitted to a polyethylene funnel. Discard the first 20 to 30 ml and collect approximately half of the solution in a weighed 600-ml polyethylene beaker. Reweigh the beaker to obtain the weight of the aliquot.

Transfer the filtered solution to a 600-ml glass beaker containing 25 ml of hydrochloric acid and 2 ml of citric acid solution. Neutralize the solution with ammonium hydroxide and add 10 ml in excess. Add 1 g of sodium cyanide and heat the solution to 55° to 60° C. Add 1 ml of hydrogen peroxide (30%) to the warm solution, and slowly add sufficient [7] 8-hydroxyquinoline solution while stirring the solution vigorously. Stir the solution vigorously for 15 min and allow the solution to stand 15 min on the edge of the steam bath. Cool the solution to room temperature, filter through a weighed close-fritted glass crucible, and wash the precipitate 10 to 12 times with water. Dry the crucible and precipitate for 1½ hr at 115° C, cool, and weigh.

4. Discussion and Results

The precipitation of aluminum with 8-hydroxy-quinoline is restricted to a somewhat narrower pH range in the presence of citric acid than is the usual case using tartaric or acetic acid. A pH-precipitation curve for aluminum hydroxyquinolate in the presence of citric acid is given in figure 1. The recoveries involve approximately 10 mg of aluminum in a volume of 150 ml, in the presence of 1 g of citric acid. Adjustment of the pH was made with ammonium hydroxide and acetic acid as indicated, and the pH was determined on a portion of the filtrate at room temperature. The first filtrate for samples run according to the recommended procedure was usually in the pH range of 9.2 to 9.4, which is a satisfactory point for complete precipitation of aluminum and nearly complete solution of molybdenum and tungsten [2]. Nickel, cobalt, iron, and chromium, the major elements, are also largely eliminated in the first precipitation.

The values obtained in table 1 show that aluminum in amounts from 10 to 100 mg (corresponding to 0.5 to 5% on the aliquot used) can be determined by the recommended procedure with an error of

the order of 1 percent of the amount present. The values obtained for aluminum in amounts below 10 mg (5 mg or less in the final aliquot) almost always indicated a negative bias, and the method as written is not satisfactory for alloys containing less than 0.5 percent aluminum. These data also show that titanium at the 2-percent level is not an interfering constituent.

The data in table 2 demonstrate that niobium, tantalum, molybdenum, tungsten, vanadium, phos-
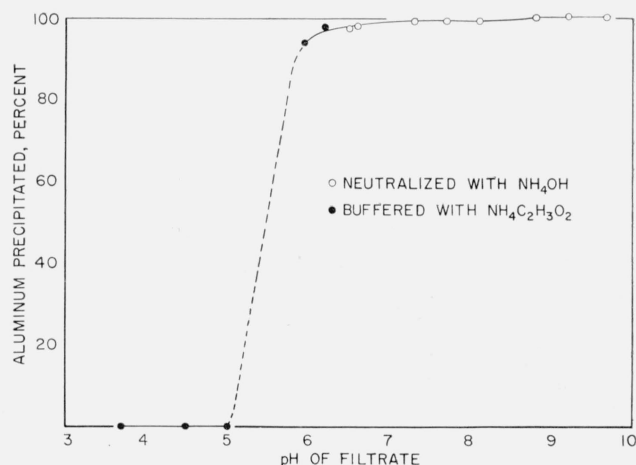

FIGURE 1. *Effect of* pH *on the precipitation of aluminum with 8-hydroxyquinoline in the presence of citric acid.*

TABLE 2. *Results of determinations of aluminum by the recommended procedure in the presence of possible interfering elements*

Sample number [a]	Weight of sample	Other element added [b]	Aluminum			
			Added	Present	Found	Difference
	g	*mg*	*mg*	*mg*	*mg*	*mg*
169	2	35 Nb	20.0	21.9	22.1	+0.2
169	2	35 Nb	20.0	21.9	21.8	−.1
169	2	84 Nb	20.0	21.9	22.0	+.1
169	2	82 Mo	20.0	21.9	21.9	.0
169	2	1 P	20.0	21.9	21.9	.0
169	2	10 Sn [c]	20.0	21.9	22.1	+.2
169	2	10 Sn [d]	20.0	21.9	22.1	+.2
169	2	10 Sn [e]	20.0	21.9	21.8	−.1
169	2	10 V	20.0	21.9	22.0	+.1
169	2	119 W	20.0	21.9	21.9	.0
169	2	5 Zr	20.0	21.9	21.9	.0
168	2	----------	20.0	20.4	20.3	−.1
168	2	----------	20.0	20.4	20.7	+.3

[a] NBS Standard Sample. Standard Sample 168, Cr 20, Co 41, Ni 20, Mo 4, W 4, Nb 3, Ta 1.
[b] All samples contain an addition of 40 mg of Ti.
[c] Tin added as metal at start.
[d] Tin added to solution of ignited oxides.
[e] Tin added as solution to caustic filtrate.

[7] Each mg of aluminum in the aliquot requires approximately 0.22 ml of 8-hydroxyquinoline solution. A small excess, 2 ml, is added to minimize absorption of excess reagent by the precipitate.

TABLE 3. *Results of determination of aluminum by the recommended procedure in high temperature alloys*

NBS standard sample	Aluminum				No. of determinations	Wt of sample	Type of alloy
	Certificate value	Found	Difference	Range			
	%	%	%	%		g	
349	1.23 [a]	1.23	0.0	1.22 to 1.23	6	2	Ni 57, Cr 20, Co 14, Mo 4, Ti 3, Al 1.
1188	0.77 [a]	0.76	−.01	0.76 to 0.77	3	2	Ni 73, Cr 15, Ti 2, Nb 1.
1189	1.20 [a]	1.17	−.03	1.17	3	2	Ni 73, Cr 20, Ti 2.5.
1191	1.55 [a]	1.54	−.01	1.51 to 1.55	8	2	Ni 55, Cr 19, Co 14, Mo 5, Ti 3.
1192	1.06 [a]	1.06	.0	1.06 to 1.07	5	2	Ni 57, Cr 18, Co 11, Mo 7, Ti 3.
106A	1.08	1.10	+.02	1.08	1	2	Nitriding steel.

[a] Provisional certificate values.

phorus, tin, and zirconium in amounts apt to be encountered in these alloys do not interfere. The use of NBS Standard Samples 168 and 169 as base material for the preparation of synthetic mixtures show that major amounts of nickel, cobalt and chromium do not interfere. A few values obtained on several high temperature alloys are tabulated in table 3, to show the agreement which can be expected on replicate determinations. The single run on the steel standard 106a is given to show that major amounts of iron do not interfere, but is not otherwise pertinent because simpler methods are available for this type of alloy.

5. References

[1] H. A. Bright and R. M. Fowler, BS J. Research **10,** 330 (1933).
[2] H. R. Fleck and A. M. Ward, Analyst **58,** 388 (1933); **62,** 378 (1937).
[3] T. Heczko, Chem. Ztg., **58,** 1032 (1934).
[4] G. E. F. Lundell and J. I. Hoffman, Outlines of methods of chemical analysis, p. 82. (J. Wiley and Sons, Inc., New York, N.Y., 1938).
[5] G. E. F. Lundell and H. B. Knowles, BS J. Research **3,** 93 (1929).
[6] E. C. Pigott, Iron and Steel **16,** 325 (1943).
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Publications of the National Bureau of Standards *

Selected Abstracts

Theory of diffraction in microwave interferometry, D. M. Kerns and E. S. Dayhoff, *J. Research NBS* **64B,** *No. 1, 1 (1960).*

Microwave Michelson and Fabry-Perot interferometers are respectively considered as instances of (1) a "reflection system," consisting of a radiating-receiving system and a reflecting object (e.g., a finite mirror) and (2) a "transmission system," consisting of a radiating system and a receiving system with an object (e.g., a Fabry-Perot etalon) interposed. The basic theoretical objective is the calculation of the amplitude and phase of the (time-harmonic) received signal in the systems considered. The electromagnetic field in space transmission paths is represented in terms of continuous angular spectra of vectorial plane waves, and the elements of the systems are described by means of suitable tensor scattering matrices (having both discrete and continuous indices). Needed scattering matrices are considered known; relationships to experimentally determinable data are outlined. The general case of either the reflection or transmission system is soluble formally in terms of a series of integrals stemming from the Liouville-Neumann series solution of certain integral equations. Formulas are obtained for models of the Michelson and Fabry-Perot instruments with arbitrary radiating and receiving characteristics. The theory and various features of the instruments considered, including Fresnel-region (or quasi-optical) behavior, are illustrated by means of examples obtained by choosing relatively simple and rather hypothetical analytical expressions for the radiating and receiving characteristics.

Some solutions for electromagnetic problems involving spheroidal, spherical, and cylindrical bodies, J. R. Wait, *J. Research NBS* **64B,** *No. 1, 15 (1960).*

Solutions are presented for the low-frequency electromagnetic response of an oscillating magnetic dipole by conducting bodies of simple shape. The quasi-stationary approximation is employed throughout which is valid when the relevant dimensions of the problem are all small compared to the free-space wavelength. This amounts to matching solutions of the wave equation within the bodies to solutions of Laplace's equation outside.

Standard free-air chamber for the measurement of low energy X-rays (20 to 100 kilovolts-constant potential), V. H. Ritz, *J. Research NBS* **64C,** *No. 1, 49 (1960).*

A description of the new National Bureau of Standards "low" energy free air chamber is given. The standard chamber is designed to measure the exposure dose in roentgens for X-ray beams generated at potentials from 20 to 100 kvcp with filtrations ranging from 2 mm of beryllium to 2 mm of beryllium plus 4 mm of aluminum. The chamber has been compared with the National Bureau of Standards medium energy standard at 60, 75, and 100 kvcp with filtrations of 3, 3, and 4 mm of aluminum, respectively. The two standard chambers agreed to within 0.3 percent.

Transmittance of materials in the far infrared, E. K. Plyler and L. R. Blaine, *J. Research NBS* **64C,** *No. 1, 55 (1960).*

The transmittance of several crystal materials with thicknesses of about 5 mm has been measured from 17 to 55 μ. The crystals are sodium chloride, potassium chloride, potassium bromide, thallium bromide-iodide, cesium bromide, and cesium iodide. Also the transmittance of polyethylene containing carbon black has been measured to 100 μ and an example of its use as a filter for far infrared is given.

X-ray attenuation coefficients from 10 kev to 100 Mev, R. T. McGinnies, *NBS Circ. 583 Suppl.* *(1959) 15 cents.*

A revision is given of the X-ray attenuation coefficients presented in National Bureau of Standards Circular 583. Table 4 of that publication is eliminated, and a new table is given for each material for photon energies less than 100 kev. The uncertainties in the estimates of attenuation coefficients at low energies are from 3 to 5 percent, which is the same as was previously given at higher energies. The cross sections for scattering are unchanged. Two values are listed for the photoelectric cross section, one calculated from the Sauter-Stobbe formulas and the other derived from new experimental evidence. The procedures for smoothing experimental data are described and are generally the same as were used in Circular 583. In addition to the systematic coverage of the region from 10 kev to 100 Mev, some data are included for a number of elements based on experimental measurements below 10 kev and above 100 Mev. A comparison is made between calculated and experimental total attenuation coefficients at energies above 10 Mev.

Photographic dosimetry at total exposure levels below 20 mr, M. Ehrlich and W. L. McLaughlin, *NBS Tech. Note 29 (PB151388) (1959) 50 cents.*

Assemblies of commercial photographic material sandwiched between two plastic scintillators can be used to measure high-energy X- or gamma-ray exposures down to 1 mr and less. The energy dependence of the assemblies' response is much less than that of a conventional photographic dosimeter, in some instances allowing an exposure interpretation with an accuracy of ± 25 percent over the energy range from about 0.1 to 1.25 Mev. However, low-intensity reciprocity failure limits the range of applicability of the system.
Conventional photographic dosimeters, not incorporating scintillators, are usually preferable for routine personnel dosimetry. By extending the monitoring period, it may be possible to avoid personnel dosimetry below 20 mr entirely. However, by doing this, one introduces additional difficulties because of instabilities in the photographic image. In some instances, an increase in effective emulsion thickness, achieved by using stacks of identical films, may lead to an increase in emulsion sensitivity sufficient to extend the useful range of a film badge well below 20 mr, without the use of a scintillator.

Variation of the thermodynamic ideal temperature in the polystyrene-cyclohexane system, D. McIntyre, J. H. O'Mara, and B. C. Konouck, *J. Am. Chem. Soc.* **81,** *3498 (1959).*

The second virial coefficients of cyclohexane solutions of several fractions of polystyrene prepared in slightly different ways have been determined by light scattering and osmometry near the theta, or ideal, temperature. The results indicate that the ideal temperature is increased as the molecular weight is decreased. The larger increase is due to small but increasingly effective chemical interactions when an *n*-butyl mercaptan group is incorporated in the chain. A much smaller effect appears to exist even when the chain is apparently uniform.

Energy dissipation in standing waves in rectangular basins, G. H. Keulegan, *J. Fluid Mech.* **6,** *Pt. 1, 35 (1959).*

The modulus of decay of standing waves of finite height is derived by assuming that the attenuation of the waves is due to viscous losses in boundary layers close to the solid walls. Dampings are observed in six basins of varying sizes. The basins are duplicated using glass and lucite for the wall materials. With liquids wetting the walls, the losses due to viscosity are slightly increased from causes presumably related to surface tension. With a liquid not wetting the walls (distilled water and lucite), losses from surface activity, of some obscure origin, outweigh many times the losses due to viscosity in the basins of smaller sizes. For moderately large basins, for which surface activity may be neglected, the agreement between the observed and computed rates of decay is found to be satisfactory.

Total photoelectric cross sections of copper, molybdenum, silver, tantalum, and gold at 662 kev, W. F. Titus, *Phys. Rev.* **115,** *No. 2, 351 (1959).*

The photoelectric cross sections have been measured for the elements Cu, Mo, Ag, Ta, and Au using the 662 kev gamma rays from Cs^{137}. The method involved the detection of the photoelectrons in a 4π geometry. The results obtained for the cross sections have an accuracy of about $2\frac{1}{2}\%$ and are in agreement with the values obtained from Grodstein.

Strength of synthetic single crystal sapphire and ruby as a function of temperature and orientation, J. B. Wachtman and L. H. Maxwell, *J. Am. Ceram. Soc.* **42,** *No. 9, 432 (1959).*

The modulus of rupture of sapphire single crystals was determined as a function of temperature for specimens with orientations favoring plastic deformation and for specimens with unfavorable orientations. From 600° C to 1000° C, the strength of both types increased with increasing temperature, but the increase was more pronounced for the former. Ruby specimens oriented favorably for plastic deformation also showed a large increase in strength. It is conjectured that the increase in strength results from stress relief by microscopic plastic deformation.

PILOT, the NBS multicomputer system, A. L. Leiner, W. A. Notz, J. L. Smith, and A. Weinberger, *Proc. Eastern Joint Computer Conf. (Philadelphia, Pa.), p. 164 (1958).*

At NBS a new large-scale digital system has been designed for use on a wide variety of experimental applications ranging from automatic search and interpretation of Patent Office records to real-time control of commercial aircraft traffic. Because of this wide range of intended use, the system had to combine in a single installation a variety of characteristics not ordinarily associated with one facility, namely (1) a high computation rate, (2) highly flexible control capabilities for communicating with the outside world, and (3) a wide repertoire of internal processing formats. The overall system is organized around three independently programmed computers which intercommunicate in such a way as to permit all three to work together concurrently on a common problem, each computer working on the piece of the problem for which it is individually best suited. The overall system thus provides a working model of an integrated multi-computer network.

Dimensional changes in systems of fibrous macromolecules: polyethylene, L. Mandelkern, D. E. Roberts, A. F. Diorio, and A. S. Posner, *J. Am. Chem. Soc.* **81,** *4148 (1959).*

Fibrous polyethylene of extremely high axial orientation was crosslinked by means of ionizing radiation, and the anisotropic changes in length that occur as a consequence of this process were investigated. In accord with theoretical expectations and with previous results obtained in a study of fibrous natural rubber, the length in the isotropic state subsequent to the crosslinking process increases as the crosslinking level increases. However, because of the initially higher axial orientation possessed by the polyethylene fibers much greater elongations are observed in the liquid state in this instance. As a consequence of this fact, on subsequent recrystallization a preferential axial crystalline orientation develops without the application of any external force. The melting and recrystallization of these fibers results in a reversible contractile system without the necessity of maintaining any external force. Anisotropic reversible dimensional changes of about 25% are observed, and these results are explicable on the basis of well established physical-chemical principles appropriate to macromolecular systems. These principles are then invoked to explain many of the observed anisotropic dimensional changes that occur in systems of naturally occurring fibrous proteins.

Attenuation of scattered cesium-137 gamma rays, F. S. Frantz, Jr., and H. O. Wyckoff, *Radiology* **73,** *No. 2, 263 (1959).*

Broad beam attenuation curves of the scattered radiation from teletherapy sources are necessary in designing secondary protective radiation barriers. Such attenuation curves in both Pb and concrete were obtained for a Cs^{137} source. Comparisons with the work of Dixon, et al., have also been made.

Photoproton cross sections of carbon, S. Penner and J. E. Leiss, *Phys. Rev.* **114,** *No. 4, 1101 (1959).*

The partial (γ,p) cross section of carbon in which the residual boron nucleus is left in the ground state has been measured with a thin-crystal proton spectrometer. This cross section is shown to decrease from about 10 mb at the giant resonance peak (22 Mev) to about 0.1 mb near 60-Mev photon energy. Angular distributions measured at five energies exhibit an asymmetry around 90° which increases rapidly with increasing energy. The partial cross section to the first excited state of boron is $(7\pm16)\%$ of the ground-state cross section. The partial cross section to one or more excited states of boron about 5 Mev above the ground state is comparable with the ground-state cross section above 30-Mev photon energy. In addition to the cross-section data, the measurements provide a sensitive means of calibrating the energy scales of electron accelerators at energies in the 25- to 50-Mev region.

Cryogenic engineering of hydrogen bubble chambers, B. W. Birmingham, D. B. Chelton, D. B. Mann, and H. P. Hernandez, *ASTM Bull. No. 240, 34 (TP164) 1959.*

Low-temperature material problems encountered during the development of a liquid-hydrogen bubble chamber are discussed. Properties affecting the selection of the bubble chamber material, the glass window, and the thermal radiation shield are examined. Methods of sealing the glass window to the chamber with various gaskets suitable for use at liquid hydrogen temperature ($-423°$ F) are presented. In addition, a method of continuously maintaining the bubble chamber and contents at liquid hydrogen temperature by means of an external refrigerator is described.

Memorandum on a procedure for obtaining spectral radiant intensities of tungsten-filament lamps, 400–700 mμ, L. E. Barbrow, *J. Opt. Soc. Am. Letter to Editor* **49**, *No. 11, 1122 (1959).*

A procedure is described for computing from the candle-power and color temperature of a tungsten-filament lamp, its spectral radiant intensity in the wavelength region 400 to 700 millimicrons. A table of spectral radiant intensities per candela for seven color temperatures is included.

Paramagnetic resonance spectra of active species. Blue material from hydrazoic acid, W. B. Gager and F. O. Rice, *J. Chem. Phys.* **31**, *No. 2, 564 (1959).*

The products of hydrazoic acid that have been decomposed thermally, electrically, and photochemically have been collected and maintained at 77° K. While at this temperature, paramagnetic resonance spectra of the samples were taken, and the result in each case was a single line at g=2.003±.002. The thermally decomposed sample showed a line width of 36 gauss while the other two samples both gave a line width of 11.5 gauss. In all three cases the lines were assymetric with the low field side of the lines being broader and less intense than the high field side. The resonance spectra is compared to the optical spectra taken of similarly prepared samples. The authors believe that a mechanism similar to an *F*-center in an alkili-halide gives rise to the resonance and to the blue color.

On prediction of system behavior, J. R. Rosenblatt, *Proc. of the New York Univ.–Ind. Conf. on Reliability Theory (New York, N.Y.) p. 39 (1958).*

It is customary in theoretical discussions of prediction of system performance to assume that the relation between variables by which performance is assessed and variables describing the parts of the system can be specified by a function. The purpose of this paper is to consider some of the problems which arise in choosing the form of such a function and in specifying the relevant variables and the nature of appropriate experiments, measurements, and data.
In the context of each of a number of familiar types of mathematical model, the possible consequences of alternative choices of time units, subsystem definitions, and independence assumptions are discussed.

Argon deposition on a 4.2° K surface, S. N. Foner, F. A. Mauer, and L. H. Bolz, *J. Chem. Phys.* **31**, *No. 2, 546 (1959).*

An uncollimated beam of argon atoms was directed onto a liquid-helium-cooled surface in such a way that the incident flux could be calculated from the gas input and the geometry. The mass per unit area of the argon film was determined by measuring the attenuation of an X-ray beam diffracted by the gold substrate.
The probability of a molecule sticking on impact was calculated from the ratio of the measured mass per unit area to the integrated mass flux on the target. The value obtained for argon deposited on argon at 4.2° K was 0.60±0.06.

Kinetic equation for a plasma with unsteady correlations, C. M. Tchen, *Phys. Rev.* **114**, *394 (1959).*

As a generalization of the Boltzmann equation, the kinetic equation for a plasma is derived in the form of a generalized Fokker-Planck equation, by considering unsteady correlations, including non-Markovian and nonlinear behavior. Both the binary and ternary correlations are used for many kinds of particles with different temperatures. The coefficients of the kinetic equation depend on the law of interaction for a pair of particles and are influenced by relaxation. The effective potential of friction consists of two parts: the static part corresponds to the Debye potential and is isotropic, the dynamical part is axially symmetrical about the direction of motion and causes a dynamical friction. The results show that the friction is proportional to velocity for slow particles, and inversely proportional to the square of velocity for fast particles. This tendency of the fast particles to overcome repulsion is a property connected with the "run-away" of electrons. A criterion for maximum friction is derived. The triplet interaction, which mainly affects the shielding phenomena, assures the convergence of the coefficients in case of distant interaction. Since the length scales of interaction are well determined in this way, the kinetic equation can be expected to be valid over a longer range than does the Boltzmann equation. The large scale agrees with the Debye radius, when the shielding term is linearized, as should be expected. When time relaxation is left aside and linearization is made, the kinetic equation degenerates to the classical Fokker-Planck equation with convergent coefficients.

Spectral study of a visible, short-duration afterglow in nitrogen, B. E. Beale, Jr., and H. P. Broida, *J. Chem. Phys.* **31**, *No. 4, 1030 (1959).*

In the discharge products of rapidly flowing, pure nitrogen at pressures between 4 and 15 mm Hg, an afterglow differing from the usual Lewis-Rayleigh afterglow has been found to occur approximately 5 milliseconds after the discharge. This pink-colored afterglow persists for about 2 milliseconds and is both preceded and followed by the usual yellow glow of active nitrogen. In the visible and near ultraviolet, this short-duration glow is characterized by strong emission of N_2+ and N_2 1st positive bands and weak emission of N_2 2nd positive bands. The vibrational intensity distributions of the bands are similar to that of the discharge, including strong emission from vibrational levels above the predissociation limit of the $B\,^3\Pi_g$ state. The existence of this afterglow shows the presence of highly energetic species other than nitrogen atoms after the discharge.

Cavity resonators for dielectric spectroscopy of compressed gases, H. E. Bussey and G. Birnbaum, *Rev. Sci. Instr.* **30**, *800 (1959).*

Convenient tunable sealed-off cavity resonators are described at frequencies of 1, 2, 9, and 24 kMc, for use with internal pressures up to 1000 psi. The modes of oscillation employed were TE_{01n}, TE_{11n}, and TM_{01}-hybrid, all in a circular cylinder. A convenient method for sealing an iris, applicable over a wide frequency range, was to insert a tapered Teflon plug. A Kovar-glass seal for coaxial lines is described that provides a good impedance match in a 50-ohm line. A brief summary of the measuring procedure is given, including a method of calibrating the cavity which increases considerably the accuracy of the loss measurements.

Dynamic stability of frozen radicals. II. The formal theory of model, J. L. Jackson, *J. Chem. Phys.* **31**, *No. 3, 722 (1959).*

In Part I, a model for frozen radical chain reactions of nitrogen atoms in a nitrogen molecule lattice was described. Here, a formal mathematical theory of these reactions is developed and applied. The results of the model are used to discuss the stability of frozen radical mixtures as a function of size. The theory also is used to obtain curves of free radical concentrations as a function of time when radicals are produced by irradiation of the solid at low temperatures. The formulas obtained are compared with most recent experimental results.

Method of cooling head-on photomultipliers, G. C. Harman, *Rev. Sci. Instr.* **30**, *No. 8, 742 (1959.)*

A simple method of cooling the photoemissive surface of head-on photomultipliers is described. It consists of a small, specially constructed dewar with a window in its top. The dewar is charged with dry ice powder and slipped over the head of the multiplier so that it cools only the sensitive surface. The rest of the tube remains at room temperature. The dark current is reduced by a factor of at least 500.

Nonresonant microwave absorption and electric dipole moment of NO in the gaseous state, A. A. Maryott and S. J. Kryder, *J. Chem. Phys.* **31**, *No. 3, 617 (1959).*

The microwave absorption in NO has been measured by a resonant cavity method at frequencies near 9 and 23 kMc/sec and at pressures in the range 3 to 27 atmos. The major part of the absorption is due to direct Λ-type doublet transitions, although at the higher pressures, a significant contribution also comes from the low frequency wings of the pure rotational spectrum. Since the Λ-doublet separation is much smaller than the applied frequency for all significant transitions, the resulting spectrum has the nonresonant or Debye shape. From the intensity of this spectrum, the electric dipole moment was found to be 0.148 ± 0.002 debye. The effective collision cross section for random spacial reorientation of the molecules is approximately twice the kinetic collision cross section.

Bremmstrahlung cross-section formulas and related data, H. W. Koch and J. W. Motz, *Rev. Modern Phys.* **31**, *No. 4, 920 (1959).*

The present report is intended to provide a coherent summary of the bremsstrahlung cross section formulas and related data. The theoretical formulas and their specific limitations are presented in a form that is most convenient for practical calculations. In addition, estimates are given for the accuracy of these formulas for cases where comparisons can be made with experimental results. Correction factors that are available are indicated in either numerical or analytical form. A brief summary of other data pertaining to electron-electron and to thick target bremsstrahlung is also included.

The nova outburst. III. The ionization of hydrogen gas by an exciting star, J. Jefferies and S. Pottasch, *Ann. Astrophys. J.* **22**, *318 (1959).*

All quantitative nova observations for the six best observed novae are brought together and an attempt is made to explain the varied observations on the basis of a consistent model. It is shown that an ejected shell may explain both the quantitative radiative emission in the lines and the initial cooling observed in both the lines and in the continuum. For the six novae considered, the density of the shell and electron temperature in the shell are found as a function of time. The temperature and radius of the central star are also found as a function of time, and the composition of the shell is also determined.

Exploratory study, by low temperature X-ray diffraction techniques, of diborane and the products of a microwave discharge in diborane, L. H. Bolz, F. A. Mauer, and H. S. Peiser, *J. Chem. Phys.* **31**, *No. 4, 1005 (1959).*

To test the hypothesis that free radicals may be stabilized by the formation of loose, one-electron bonds with electron deficient molecules, diborane and the products of a microwave discharge in diborane have been studied by low temperature X-ray diffraction. Two crystalline phases were distinguished in ordinary diborane. An additional phase, which may be

BH_3, was found in microwave-discharged diborane. Because rapid warm-up occurred spontaneously, starting at a temperature near 4.2° K, it cannot be concluded that diborane helped appreciably to stabilize the atomic hydrogen present in the microwave-discharge products.

The double bond isomerization of olefins by hydrogen atoms at −195°, M. D. Scheer and R. Klein, *J. Phys. Chem.* **63**, *1517 (1959).*

The focus of interest in low temperature chemistry coupled with the rather unusual nature of this low temperature reaction dictates the prompt disclosure of this information in the form of a note.

Other NBS Publications

Journal of Research, Section 64D, No. 2, March–April 1960, 70 cents.

Optimum frequencies for outer space communication. George W. Haydon.
The joint use of the ordinary and extraordinary virtual height curves in determining ionospheric layer profiles. L. R. O. Storey.
Measured statistical characteristics and narrow band teletype message errors on a single sideband 600 mile long ultrahigh frequency tropospheric radio link. E. F. Florman and R. W. Plush.
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Terrestrial propagation of very-low-frequency radio waves, a theoretical investigation. James R. Wait.
Aurora of October 22/23, 1958, at Rapid City, South Dakota. F. E. Roach and E. Marovich.

Journal of Research, Section 64B, No. 1, January–March 1960, 75 cents.

Theory of diffraction in microwave interferometry. D. M. Kerns and E. S. Dayhoff. (See above abstract.)
Some solutions for electromagnetic problems involving spheriodal, spherical, and cylindrical bodies. James R. Wait. (See above abstract.)
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A symmetric continuous poker model. A. J. Goldman and J. J. Stone.
Moebius function on the lattice of dense subgraphs. R. E. Nettleton and M. S. Green.
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Power loss and operating temperature of tires, R. D. Stiehler, M. N. Steel, G. G. Richey, J. Mandel, and R. H. Hobbs.
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