NBS

Technical Note 286

SPARK SOURCE MASS SPECTROGRAPH PROGRAM
JULY 1964 TO JUNE 1965

PAUL J. PAULSEN AND PAUL E. BRANCH

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. Its responsibilities include development and maintenance of the national standards of measurement, and the provisions of means for making measurements consistent with those standards; determination of physical constants and properties of materials; development of methods for testing materials, mechanisms, and structures, and making such tests as may be necessary, particularly for government agencies; cooperation in the establishment of standard practices for incorporation in codes and specifications; advisory service to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; assistance to industry, business, and consumers in the development and acceptance of commercial standards and simplified trade practice recommendations; administration of programs in cooperation with United States business groups and standards organizations for the development of international standards of practice; and maintenance of a clearinghouse for the collection and dissemination of scientific, technical, and engineering information. The scope of the Bureau's activities is suggested in the following listing of its three Institutes and their organizational units.

Institute for Basic Standards. Applied Mathematics. Electricity. Metrology. Mechanics. Heat. Atomic Physics. Physical Chemistry. Laboratory Astrophysics.* Radiation Physics. Radio Standards Laboratory:* Radio Standards Physics; Radio Standards Engineering. Office of Standard Reference Data.

Institute for Materials Research. Analytical Chemistry. Polymers. Metallurgy. Inorganic Materials. Reactor Radiations. Cryogenics.* Materials Evaluation Laboratory. Office of Standard Reference Materials.

Institute for Applied Technology. Building Research. Information Technology. Performance Test Development. Electronic Instrumentation. Textile and Apparel Technology Center. Technical Analysis. Office of Weights and Measures. Office of Engineering Standards. Office of Invention and Innovation. Office of Technical Resources. Clearinghouse for Federal Scientific and Technical Information.**

---

*Located at Boulder, Colorado, 80301.

**Located at 5285 Port Royal Road, Springfield, Virginia, 22171.

NATIONAL BUREAU OF STANDARDS

Technical Note 286

ISSUED APRIL 15, 1966

SPARK SOURCE MASS SPECTROGRAPH PROGRAM
JULY 1964 TO JUNE 1965

Paul J. Paulsen and Paul E. Branch

Spectrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

For sale by the Superintendent of Documents, Government Printing Office
Washington, D.C., 20402 - Price 25 cents

FOREWORD

The Analytical Chemistry Division was established as a spearate division at the National Bureau of Standards on September 1, 1963 and became part of the Institute for Materials Research in the February 1, 1964 reorganization. It consists at present of eight sections encompassing some 30 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it service analysis or standard reference material. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. In the future we plan to issue these summaries for a number of programs. The following is the second report in this series on progress of the Spark Source Mass Spectrograph program.

In preparing this report, it has been necessary to make occasional reference to existing commercial equipment. However, such mention snould in no case be considered as representing a recommendation or endorsement by the National Bureau of Standards.

W. Wayne Meinke, Chief
Analytical Chemistry Division

TABLE OF CONTENTS

2. INSTRUMENT MODIFICATIONS . . . .

4. PROCEDURE FOR SAMPLE ANALYSIS . . . .

5. EXPERIMENTAL RESULTS . . . .

LIST OF FIGURES

LIST OF TABLES

SPARK SOURCE MASS SPECTROGRAPH PROGRAM
July 1964 to June 1965

Paul J. Paulsen and Paul E. Branch

ABSTRACT

This report describes the activities of the spark source mass spectrograph project for the period from July 1964 through June 1965. The subjects covered include instrument modifications which resulted in lower backgrounds, modifications planned for the near future, an outline of the procedure used in an analysis, a description of data computation techniques, and experimental results obtained for some NBS standard reference materials. Photographs of the instrument with its modifications as well as photographs of the improved mass spectrum are also included.

1. INTRODUCTION

The radiofrequency spark source mass spectrograph has been shown in the last few years to be a useful tool for the analysis of solids for elements present down to the parts-per-billion level. Because the elemental sensitivity factors vary only about one order of magnitude, semi-quantitative analysis can be obtained without the use of standards. Reports indicate that with standards ± 20% accuracy is obtainable. A most important feature of this method of analysis is the absence of inherent blind spots; in many matrices all elements are detectable at the parts-per-billion level. The blind spots that do appear come from the matrix itself and in high purity samples are generally limited to a few elements.

During the past year work with the spark source mass spectrograph in our laboratory has been in three general categories.

a. Semi-quantitative analysis of high purity materials for elements present to the 100 ppb level.

b. Obtaining quantitative information on elemental sensitivities and instrument operation by studying standard samples.

c. Modifying the instrument in order to improve detection capabilities.

While the analysis of high purity materials could be considered to be primarily a service function, it in fact has generated part of the problems studied in b and in one way or another was the prime factor in all instrument modifications.

The quantitative studies using known samples are being made in order to build a base of information for use in future analysis. To the present, this work has resulted primarily in the development of methods of sample and data handling, and has indicated to what extent data obtained at high concentration can be used at lower concentrations. However, its most important aspect has been in the general improvement in the competence level of the technique.

All instrument modifications were made in order to improve the detection limits, not by increasing instrument sensitivity, but by removing interferences. The interferences arose from lines at specific masses caused by instrument background gases and source parts, general plate background, from poor vacuum, and too broad matrix lines.

The instrument used for these studies is a Consolidated Electrodynamics Corporation (CEC) No. 21-110 lot 4 1/2 as shown in figures 1 and 2*. The 200-liter per second ion pump on the electric sector (figure 2) was added two years ago to replace the oil diffusion pump supplied by CEC. The other items labeled in the figure were added this last year and will be described later.

2. INSTRUMENT MODIFICATIONS

A. Additional Analyzer Pumping

Poor vacuum in the electric and magnetic sectors of the instrument degrades sensitivity of analysis in two ways, both being directly proportional to the pressure in the system. Ions undergoing a change in charge upon collision with gas molecules between the magnetic and electric sectors will appear as discrete lines on the photographic plate masking specific masses. Due to the low probability of collisions at the vacuum level normally obtained, these lines are seen only for the matrix element at levels corresponding to a few parts per million.

Causing more interference are ions undergoing change of charge on collision with gas molecules in the magnetic sector. These ions cause a continuous background darkening of the

---

*In order to specify the procedures and equipment modifications adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

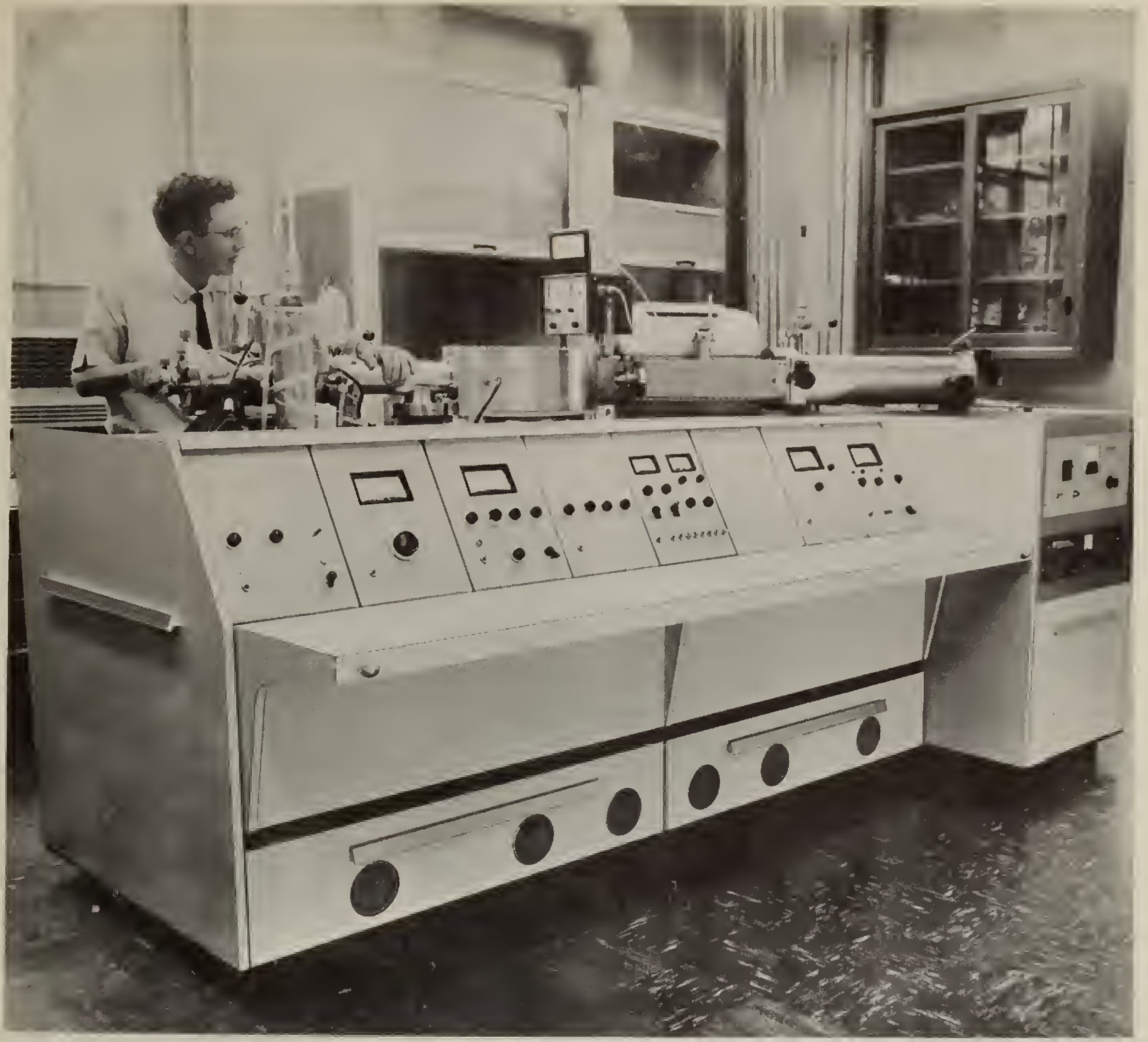


Figure 1. Spark source mass spectrograph.

photographic plate, which is darkest near the major peaks, namely the lines of plus one, two, three, etc., charged matrix ions. Normal operation of the RF spark in the source, which is separately pumped, causes pressures well into the 10^{-6} torr region which in turn significantly raises the pressure in the electric and magnetic analyzer sections. To eliminate this pressure rise in the electric and magnetic sections and the resulting increase in background, a combination titanium sublimation pump and ion pump was installed on the drift tube connecting the source to the electric sector. The pumping capacity of this unit is about 400 liters per second.

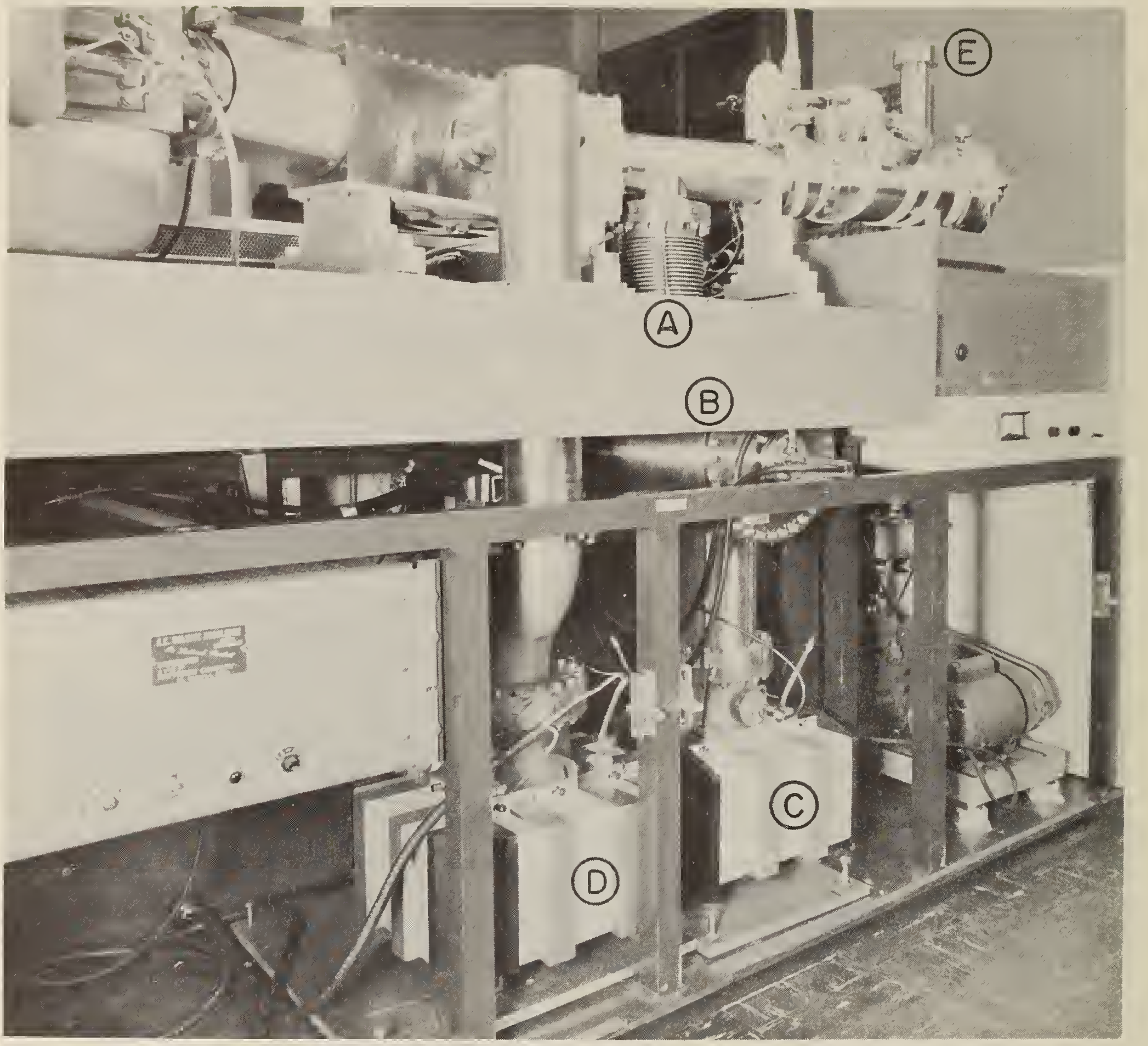
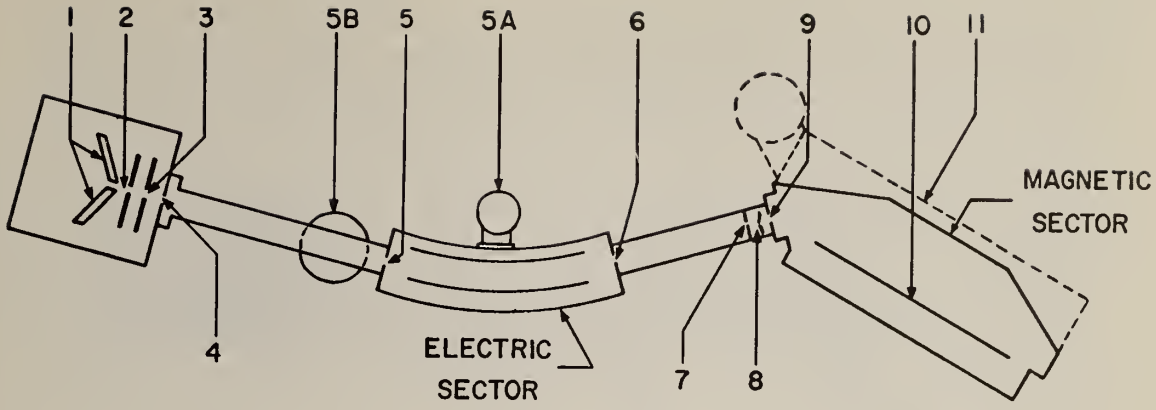


Figure 2. Rear view of instrument showing major vacuum modification. A. New pumping port. B. Titanium sublimation chamber. C. 100-liter per second ion pump. D. 200-liter per second ion pump. E. Liquid nitrogen cold finger.

No pressure rises are now detectable in the analyzer section upon sparking. This position and the pumping capacity were selected in anticipation of the future addition of a pump on the magnetic sector. See figure 2 and 5B in figure 3.



1. SAMPLE ELECTRODES
2. FIRST APERTURE
3. SECOND APERTURE
4. OBJECT SLIT
5. ELECTRIC SECTOR ENTRANCE SLIT
5A. 200 L/S ION PUMP
5B. NEW PUMPING PORT - 400 L/S
6. ELECTRIC SECTOR EXIT SLIT
7. MAGNET SHUNT
8. BEAM MONITOR ELECTRODES
9. ENERGY RESOLVING SLIT
10. PHOTOGRAPHIC PLATE MASK
11. FUTURE MAGNET PUMPING SYSTEM

Figure 3. Diagram showing position of major components of mass spectrograph.

B. Source Ion Gauge.

Gases in the source cause background lines to appear for O_2, O, N_2, N, C_2, C, CO_2, CO and hydrocarbons. In general most of the unit masses from 32 on down have interfering lines at the parts per million level originating from source gases. In order to minimize gas background lines an ion gauge was mounted on the source chamber to monitor source pressures so as to insure an adequate vacuum before an analysis was attempted. An overnight pumping after sample loading gives source pressures of 1×10^{-7} torr; with a six hour baking (overnight) of the source region at 110°C, a pressure of 1 to 2 $\times 10^{-8}$ is obtained. However, even with baking, pressures of midrange 10^{-6} are obtained upon first sparking of the sample during an analysis.

C. Cold Finger.

A liquid nitrogen cold finger was added to the source housing (figure 2) in order to remove hydrocarbon lines from the source background. The hydrocarbons originate from the oil diffusion pump used to pump the source. If liquid nitrogen is added soon after source pumping is started (with pressures of low 10^{-5} to high 10^{-6}) pressure drops of 3-to-10 fold are observed; if added to a well pumped source (low 10^{-8}) the pressure drops less than 50%. Without liquid nitrogen a well pumped source shows hydrocarbon lines equivalent to 1 ppm Fe in the iron region of the spectrum. With liquid nitrogen in the source cold finger the lines are removed to below 0.1 ppm Fe, our present detection limits.

D. Tantalum Source Parts.

Analysis of several materials having five-nines and six-nines purity indicated the presence of iron, nickel and chromium at levels too high to be credible. Since the entire instrument and specifically the source parts are made of stainless steel it was assumed that these lines represented instrument background. Since lines on the plate can only be formed for ions leaving the source with the full accelerating voltage these lines must originate from limited regions within the source.

In order to locate the source of background the most suspect parts of the source were replaced stepwise with parts fabricated from either aluminum or tantalum while noting the apparent iron, chromium, and nickel content of a high purity platinum sample. In this manner it was found that the background was due to the sample holding jaws, the first aperture (No. 2 in figure 3) and the second aperture (No. 3 in figure 3) of the source slit system. To meet this problem these stainless steel parts were replaced with tantalum parts. The instrument background now contains masses 181 (Ta^+), 182 (TaH^+), 197 (TaO^+), which interferes with gold 197 at approximately the 1 ppm level), and 213 (TaO^+_2). This background causes little difficulty in that tantalum is unlikely to be present in most samples, and if suspected the sample may be rerun using stainless steel parts. The stainless steel background appears to be removed from the spectra at our present limits of detection. However, a few tenths parts per million iron has been found in all high purity samples run using the tantalum parts and it is not known whether this represents true contaminants or some residual instrument background.

Shown in figure 4 are two equal exposures for a high purity copper sample. The upper one was made using the forementioned tantalum parts, the lower one with stainless steel parts. The iron, nickel, and chromium background lines show up at more than 10 ppm with stainless steel parts and are totally absent with tantalum parts.

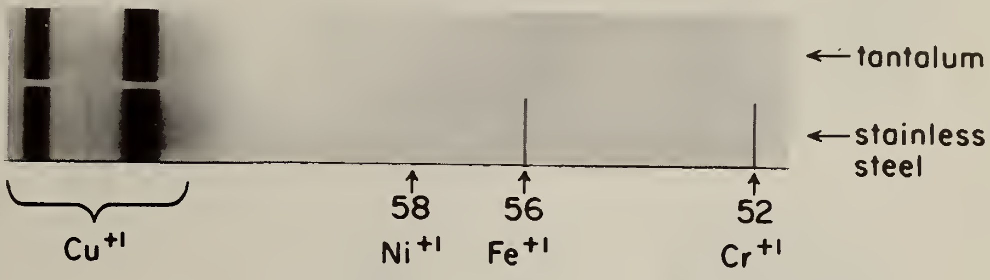


Figure 4. Background lines with stainless steel and tantalum source parts.

E. Source Apertures.

In most high purity materials a likely impurity is an element of one unit higher and/or one unit lower Z number. Thus finding one ppm of these impurities may involve detecting a line only a few mass units away from the matrix line which is a million times as intense. In this situation high resolution and low background at the matrix lines are of prime importance.

A comparison was made between the spectra for a standard size second aperture (No. 3, figure 3), which is a rectangular opening, and one of half its length. The shorter aperture resulted in narrower matrix lines for equal exposures. Other experiments with combinations of first and second aperture sizes resulted in the selection of a first aperture of a 1/8-in. diameter hole (as compared to 1/4-in. as supplied by CEC) and a second aperture 0.040 in. by 0.068 in. (as compared to 0.040 in. by 0.187 in. as supplied by CEC). This combination reduces the average ion current through the instrument by a factor of 2 to 3 and thus longer times are required to make the exposures. Figure 5 shows tantalum parts in the large and small sized apertures. The upper disks are the first apertures and the lower disks are the second apertures; the latter are tantalum inserts fitting into the stainless steel "top hat" shown on the right. (The inserts resulted from the conversion from stainless steel to tantalum apertures as previously discussed).

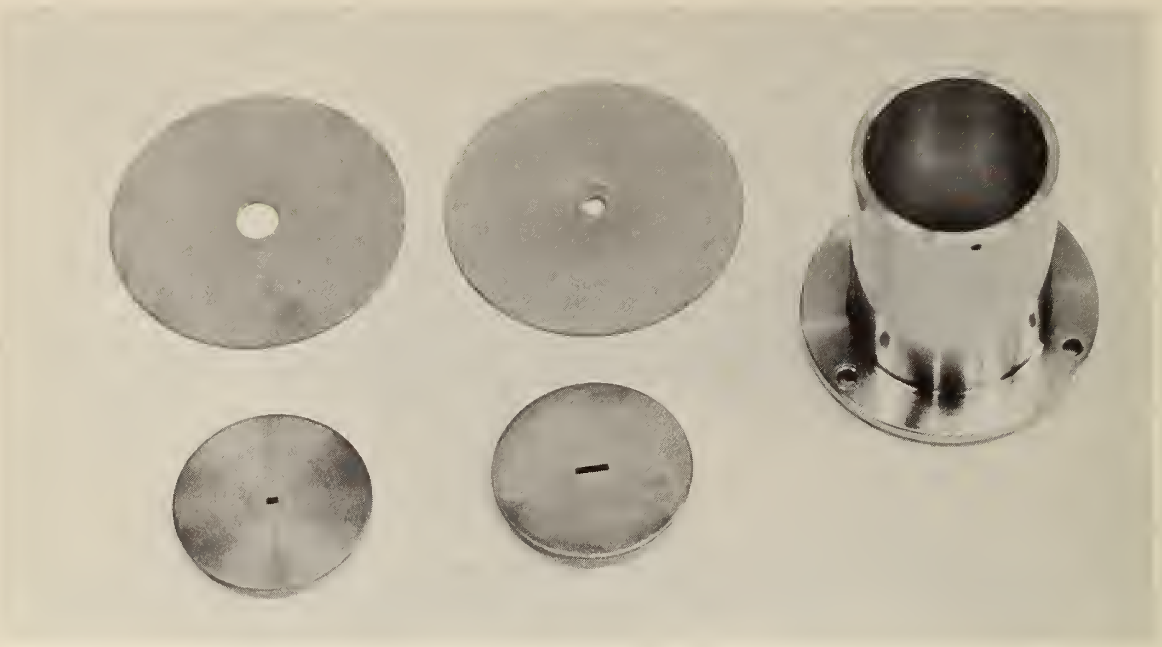


Figure 5. Large and small tantalum first and second apertures.

Figure 6 shows the plus-one platinum line of two exposures of 1.00×10^{-8} coulombs (1/10 the possible maximum exposure) made on the same sample of 99+% Pt. The exposure labeled "small" used a 1/8-in. diameter first aperture and a 0.068-in. long second aperture. The one labeled "large" used a 1/4-in. first aperture and a 0.187-in. long second aperture. The greatly improved line widths

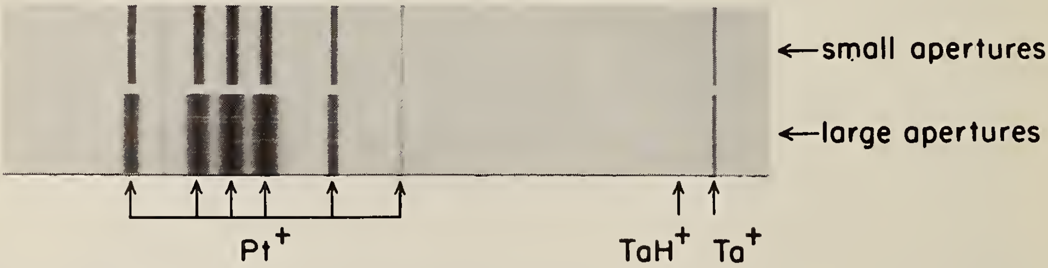


Figure 6. Equivalent exposures of Pt with large and small sized apertures.

from the small sized apertures are limited to major peaks of the matrix material (Pt), with low concentration impurity lines having essentially the same line width for both aperture sizes. The matrix line widths increase with an increase in exposure for both aperture sizes. However, ten times as heavy an exposure is necessary for the small aperture in order to obtain the same line width as with the large aperture.

3. PLANNED INSTRUMENT MODIFICATIONS

Within the next year we plan to replace our present 15-kV ion accelerator with one capable of operating at 16, 20, and 24 kV. When operated at 24 kV the sensitivity of detection for the instrument should be four times that obtained at 15 kV. This CEC conversion also includes a new electric sector power supply and in addition requires acquisition of a new source capable of handling 24 kV. At the same time wider slits will be installed throughout the instrument to give an increase in sensitivity of a factor of three. This conversion will result in a loss of resolution from our present 1 part in 2500 to 1 part in 2000. The combination of higher accelerating voltage and wider slits should result in a 12-fold increase in detection sensitivity. There will also be, however, an increase in background from ions scattered by gas molecules in the magnet as discussed previously. Additional pumping at the magnet such as shown in figure 3 at No. 11 will be needed to lower this background. The additional pumping will not be added until after the effectiveness of the change in accelerating voltage and slits widths has been evaluated.

In those areas of the mass range where our present background is below the threshold of detection for the plate, the increased background will have little if any effect in reducing the 12-fold increase in sensitivity. Where the background is presently detectable, the increased background will partially but not completely cancel the increased sensitivity.

4. PROCEDURE FOR SAMPLE ANALYSIS

A. Sample Types.

The R. F. spark source should be capable of running any type solid with a vapor pressure less than 1 x 10^{-7} torr at room temperature. Our actual experience has been with solid conductors, and with insulators using a conducting counter electrode. Present plans call for a study in the future of conducting and insulating powders pelletized with ultra pure carbon powder.

B. Sample Preparation.

Preparation depends on sample size and the type of information desired from the analysis. Identification of the major components in micron sized particles can be obtained by mounting them on the tips of ultra pure electrodes and sparking. However, surface contamination on the electrodes must be removed prior to mounting.

The ideal sample consists of two electrodes 1/2 in. long with a diameter between 0.020 and 0.050 in. Larger diameters up to 1/8 in. can be handled, but efficiency of ion collection drops off at larger sizes due to projections of the sample lying between the point where sparking occurs and the source slit. All samples must be etched just before loading into the instrument in order to remove contaminations introduced in machining and handling.

An illustration of the contamination problem was a tantalum sample cut using a spark erosion machine and then vapor degreased with trichloroethylene. Despite the use of new oil and the cleaning of the machine just before this job, the mass spectrum showed over a dozen elements above the 10-ppm level as well as hydrocarbons. This list of elements could well have been a list of materials previously cut with the machine. The tantalum sample was then removed from the instrument, etched for approximately 30 seconds in a 50-50 HF and HNO_3 mixture, and rinsed in distilled water. Upon rerunning the sample, all the elements previously seen were not detected at the 1-ppm level.

C. Running of Sample

Since increases in R.F. pulse lengths, pulse repetition rates, and voltages will all increase the power to the sample and hence its temperature, it was decided to maintain all of these factors constant during an analysis in order to avoid the change in instrument bias which might result from such temperature changes. The gap between the sample electrodes is maintained at maximum possible separation while sparking since it has been shown that, for a constant total exposure, intensity of the plus one ion (and the plus two) changes markedly with gap width, and the ratio of the one to two is more reproducible with a wide gap. The surface of the sample is presparked for an exposure of 1 x 10^{-8} coulomb in order to condition the electrodes and to remove surface contamination. A comparison of this exposure to one of equal intensity selected from the set of succeeding exposures identifies the surface contaminants. Experience indicates that a thorough prespark will reduce surface contaminants only 10 to 100 fold. For analysis of alloys where duplicate exposures are made at several exposure levels, exposures are alternated between the high and low levels.

D. Plate Development and Handling.

Plates are presently being developed using Ilford caustic hydroquinone for 2 and 1/2 minutes at 68 F. Ilford ID-19 and Kodak D-19 have also been used. However, no systematic studies on the optimum developer and conditions of development have been undertaken or are anticipated.

Ilford Q-2 photographic plates are ordered only during the winter months and are stored at 0°F in order to prevent heat fogging during shipment and storage of the plates. It is necessary, however, to allow the plates to warm up to room temperature before loading and pumping them. It was recently discovered that a longstanding, elusive but characteristic pattern of plate fogging has been caused by loading cold plates into the vacuum system. The fogging arises from the fast removal of condensed water from the cold plate emulsion upon pumping.

E. Plate Measurement and Data Calculation.

For measuring peak absorption of line images the microphotometer is adjusted for 0% absorption at the clearest portion of the plate and 100% absorption for no light. Plate calibration curves can be obtained with methods analogous to those used in emission spectroscopy. However, there are two important differences between photometry of plates used in mass spectroscopy and those generally used in emission spectroscopy. First, the maximum darkening of the mass spectrographic plate gives approximately 90% absorption while the emission spectrographic plate has a maximum darkening of essentially

100% absorption. Thus a plot of the Seidel function values for % absorption vs. log exposure, which gives a straight line calibration curve for emission spectroscopy, will give a line which curves asymptotically to the Seidel value corresponding to 90% absorption for a mass spectrographic plate. Secondly the maximum line darkening on a mass spectrographic plate varies from 80 to 90% between high and low mass, with the lower mass ions giving the darker lines. Thus the Seidel plots for high and low mass ions will curve off to different values at the 100% absorption end of the plot. Under these conditions no single calibration curve will serve for all lines on the plate.

If the percent absorption values obtained from the microphotometer for various masses are multiplied by a "stretch" factor of 100 divided by percent absorption at maximum darkening for that mass, one obtains percent absorption values from zero to 100 which will give a straight line calibration curve fitting all masses on a plate. At present, calibration curves are obtained using log intensity vs. probability function values of the stretched percent absorption. The "curve" is assumed to be a straight line and the slope of this line is calculated from the percent absorption values and the known ratio of isotopes for an element. Normally data for the slope are pooled for at least three different elements, each with a half dozen pairs of lines whose absorption values range from 10 to 90%. Because of the high scatter in the data from which comparisons must be made it has not been determined whether the probability function presently used or the Seidel function from emission spectroscopy will give the closest fit to a straight line calibration curve.

Once the slope of the calibration curve is found this information plus peak heights, peak backgrounds, and peak stretch values are fed by a Teletype unit into a computer in which the following operations are performed:

1. Calculates peak intensity and peak background values from % absorption, and subtracts to find net intensity.

2. Averages net intensity values for the duplicate exposures.

3. Calculates standard deviations (σ).

4. Rejects data differing 2σ from average and recalculates a new average intensity.

5. Calculates the ratio of the net intensity of each line measured to an "internal standard" line from the same exposure.

6. Repeats steps 2, 3, and 4 for ratios calculated in 5.

For an average plate involving the analysis of a dozen elements in an alloy there are approximately 230 peaks used to compute the results. The total time necessary with the computer calculation of this amount of data is 3 hours for punching tapes, 3 hours of Teletype time, and under 100 seconds of actual computer time. Twenty-eight hundred separate steps of addition, multiplication, squaring, etc., would be necessary to make the same calculations by hand. The use of the computer results in a saving of approximately two man days per plate, but more important is the drastic reduction of number of errors made in the calculations.

The average peak intensities and/or ratios of intensities thus calculated can be used with the isotopic abundances of the mass line measured and the relative sensitivity factors for each element to calculate the concentration of each element in the sample. When a standard sample is run, as is the case for most of the data contained in this report, the certified elemental concentrations are combined with the forementioned data to calculate relative elemental sensitivity factors.

The use of an internal standard has been adopted in these determinations of sensitivity factors in order to correct for some of the intensity fluctuations which are common to all lines. This includes fluctuations caused by errors in the measurement of total exposure, changes in the ratio of plus one to plus two ions, and changes in peak width. The effectiveness of the internal standard method is shown by the lower percent standard deviation* in the ratio of peak intensities, as compared to the percent standard deviation in the peak intensities for a given set of data.

Up to the present all data have been based upon the maximum intensity for the plus one charge state of each element. A more reliable method of analysis would be to

---

*Percent standard and deviation = coefficient of variation $= \frac{\sigma}{x} \times 100$, where σ is the standard deviation and x is the average of the results used to determine σ.

measure the total number of ions for each element which hit the photographic plate. To do this would require the summation of the peak areas over all the charge states of an element. Summation of all charge states is necessary because the distribution of ions among the charge states is dependent upon non-reproducible sparking conditions in the source. Peak areas must be measured instead of maximum intensities since peak widths and shapes are not constant. Peak shapes are irregular at low percent absorption and in regions of the plate where perfect focus is unobtainable. Peak widths change with source operating conditions and position on the photographic plate.

The extension of our present technique by measuring the percent absorption at 10 uniformly spaced positions across the peak, and a summation of the calculated intensities to give a peak area would not be of practical value because of the overwhelming increase in the number of calculations necessary per plate. In the future, data will be computed from the product of maximum peak intensity times the peak width at half intensity. This product is a good approximation to peak area, but it is sensitive to irregularities in the peak shapes.

5. EXPERIMENTAL RESULTS

A. Oxygen Isotope Ratios in Al_2O_3.

The oxygen isotope ratios in a sample of Al_2O_3 in rod form were measured in order to determine the feasibility of using the spark source mass spectrograph to analyze for oxygen 18 in a diffusion-exchange experiment with Al_2O_3 and enriched oxygen. By the use of a counter-electrode of platinum and a short piece of Al_2O_3 it was possible to obtain a satisfactory ion beam from this insulator. The isotopes of platinum were used to determine the plate calibration curve by the method described previously.

Table 1 shows the results for oxygen isotope ratios as well as some platinum ratios which were included to indicate the accuracy of the calibration curve.

It was concluded that the errors in the oxygen ratio determinations by this method were too large to be of practical value for the diffusion-exchange experiments. The errors are believed to have been caused by differences in peak widths and background lines at masses 17 and 18 $^{16}OH^+$ and $H_2{}^{16}O^+$.

Table 1. Isotopic ratios of oxygen in Al_2O_3 and platinum ratios.

	Experimental value		True value	Error[a]
Oxygen 16/17	2010	±20%[b]	2667	25%
Oxygen 16/18	299	±17%	488	38%
Oxygen 17/18	0.151	± 7.4%	0.183	17%
Platinum 196/198	3.65	±11%	3.51	4.0%
Platinum 195/198	5.03	±12%	4.69	7.3%
Platinum 194/196	1.33	± 6.7%	1.30	2.3%

---

[a] Difference expressed in percent.
[b] Percent standard deviation.

B. Cartridge Brass.

Analyzed samples have been run primarily to determine if sensitivity factors determined at high concentration levels can be applied at low levels. A secondary purpose is to have sensitivity factors available for various matrices for semiquantitative analysis, and to see if the sensitivity factor of a given element changes with matrix. The sensitivity factors reported are per unit weight (not atomic) and have been determined using peak heights but not peak widths. These are preliminary results from sparking a single loading of each sample. The final results will be based on three sets of duplicate analyses, each with new sample electrodes, for all the standards in this series, C1100, C1101, C1102.

In Table 2 are shown the sensitivity factors of samples C1100 and C1102 determined for each element using an internal standard of lead (sensitivity factor of lead = 1.000). In addition, the data from C1102 were combined with the sensitivity factors determined for C1100 to calculate an analysis of C1102. The NBS certified analysis of C1102 is included for comparison. The inherent difficulty in using one element for an internal standard is that erroneous results for it in either the standard sample or the "unknown" sample will cause a constant error for all the elements in the "unknown" sample. This effect is probably the cause of the consistently low results determined for C1102.

Table 2. Mass spectrographic sensitivity factors for NBS cartridge brasses C1100 and C1102; experimental analysis of C1102.

	Sensitivity factors		Analysis of C1102	
	C1100	C1102	Experimental value Weight percent	NBS certified value Weight percent
Pb	1.000	1.000	---	---
Al	40	(11)?	0.00019	0.0007
P	27			
Fe	3.08	2.2	.0078	.011
Mn	0.60	0.37	.0028	.0045
Ni	1.98	1.4	.0037	.005
As	5.0	3.7	.0029	.004
Ag	1.09	1.01	.00093	.0010
Cd	4.5	3.15	.0031	.0045
Sn	1.16	1.2	.0063	.006
Sb	2.1	1.8	.0045	.005
Te	2.4			
Bi	0.90	0.85	.00047	.0005

C. Tin NBS 431 to 435.

During the analysis of a high purity tin sample it became necessary to determine the sensitivity factors of several elements found in the tin in order to give qualitative data. The NBS tin standards 431 through 435 contained the elements of interest. When sensitivity factors for both 431 and 435 were obtained, conflicting results showed up for copper, one of the elements of interest. It was decided therefore to determine the sensitivity factors for as many elements as practical in the whole series to see if other elements acted in the same way. In general when going from 431 to 435 there is a 20-fold decrease in elemental concentrations. The data represents multiple exposures on a single plate from a single pair of sample electrodes. During the period when this data was collected considerable trouble was encountered with uneven fogging of the plates as discussed previously.

Table 3 lists the percent standard deviation of peak intensities and the percent standard deviation in the ratio of peak intensity to the intensity of the arsenic peak on the same exposure. The lower deviations for the ratio values indicate the effectiveness of the "internal standard" in moderating intensity fluctuations. The

Table 3. Comparison of sensitivity factors computed with and without the use of an internal standard.

	Precision of measurements		Calculated sensitivity factors	
	Intensity	Ratio	From ratio	From intensity
Cu 63	20%[a]	8.6%[a]	2.23	2.23
Cu 65	21	7.2	2.21	2.23
Zn 66	32	26	20.1	20.2
Zn 67	23	16	20.5	20.5
Zn 68	31	26	19.3	19.3
As 75	17	--	1.000	1.000
Sb 121	20	6.3	0.365	0.367
Sb 123	20	12	.377	.377
Pb 207	20	14	.594	.593
Pb 208	21	10	.601	.604
Bi 209	26	13	.876	.888

---

[a] Percent standard deviation.

sensitivity factors, however, indicate that it makes little difference whether average intensities or peak ratios are used in the calculation.

Table 4 lists the isotope ratios determined from the same data used for table 3 for various elements together with the true value. The differences indicate how well the calibration curve fits the plate. The standard deviations should represent only the nonuniformity in the photographic plate and errors in reading the plate absorption. The data indicate that the photographic plate will ultimately limit the accuracy of analysis to a 3 to 5 percent error.

Table 4. Comparison of experimentally determined isotope ratios with true values

Isotopes	True ratio	Experimental ratio
Cu 63/65	2.235	2.249 ± 4.6%[a]
Zn 66/68	1.498	1.554 ± 2.3
Zn 67/68	0.2213	0.2131 ± 2.1
Cd 110/111	.9718	.9844 ± 3.8
Sb 121/123	1.339	1.309 ± 9.0
Pb 207/208	0.4321	0.4258 ± 7.6

---

[a] Percent standard deviation.

Listed in Table 5 are all the sensitivity factors determined for the series 431 through 435. Only on number 431 was a duplicate determination made. Arsenic, the arbitrarily chosen internal standard, has been assigned a sensitivity factor of 1.000 for all samples. Copper has a sensitivity factor which increases with a decrease in concentration (431 to 435) while the sensitivity of zinc decreases with a decrease in concentration. All other elements show no trends with a change in concentration. Excluding copper and zinc the maximum deviation of the sensitivity factors from the average is less than +45 and -44 percent.

Table 5. Sensitivity factors for elements in tin using As for an internal standard with an arbitrary sensitivity of 1.000.

	Cu	Zn	As	Cd	Sb	Pb	Bi	Ag
431 A	1.81	21.1	1.000	3.56	0.290	0.388	0.454	--
431 B	1.09	16.7	1.000	2.38	.214	.294	.450	0.348
Average	1.45	18.9	1.000	2.97	.253	.341	.452	.348
432	2.21	24.5	1.000	4.77	.465	.726	.984	.657
433	2.27	19.3	1.000	4.60	.371	.584	.847	.599
434	3.91	11.5	1.000	6.74	.471	.804	1.10	.661
435	5.37	5.02	1.000	4.23	.426	.463	.636	--
Average	--	--	1.000	4.66	.391	.584	.804	.566
Maximum deviation from the average				+45% -36	+20% -36	+38% -41	+37% -44	+17% -39

Since the choice of arsenic as the internal standard was completely arbitrary and since it was also noted that the sensitivity of antimony followed the changes in the other elements, all the data in table 5 were recalculated with respect to antimony. This was done by simply dividing the sensitivity factors in each row by the value for antimony. The results of this conversion are shown in Table 6. Copper and zinc still show the same trends, but now the maximum deviations from the average sensitivity factors are less than 25%, if only one piece of arsenic data is omitted.

Table 6. Elemental sensitivity factors in tin with Sb arbitrarily assigned a sensitivity factor of 1.000.

	Cu	Zn	As	Cd	Sb	Pb	Bi	Ag
431 A	6.23	72.7	3.45	12.3	1.000	1.18	1.56	--
431 B	5.09	78.0	4.67	11.1	1.000	1.37	2.10	1.63
Average	5.66	75.3	4.06	11.7	1.000	1.27	1.83	1.63
432	4.75	52.7	2.15	10.2	1.000	1.56	2.04	1.41
433	6.12	52.0	2.695	12.4	1.000	1.57	2.28	1.61
434	8.30	24.4	2.12	14.3	1.000	1.71	2.33	1.40
435	12.6	11.8	2.35	9.96	1.000	1.09	1.49	--
Average			2.67	11.7	1.000	1.44	1.99	1.51
Maximum deviation			+52%	+22%		+19%	+17%	+8%
from the average			-21	-15		-24	-25	-7.3

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMME