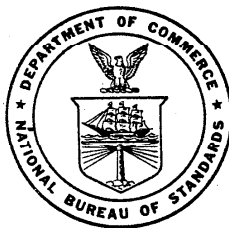




NBS MISC. PUBL. **260-5**

Standard Reference Materials:

**Accuracy of Solution X-Ray Spectrometric
Analysis of Copper-Base Alloys**



**U.S. Department of Commerce
National Bureau of Standards**

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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

OTHER NBS PUBLICATIONS OF INTEREST

NBS Misc. Publ. 260, Standard Reference Materials: Catalog and Price List of Standard Materials Issued by the National Bureau of Standards, January 1965. In press.* (Supersedes NBS Misc. Publ. 241, March 1962.)

NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, June 1964. 30 cents.*

NBS Misc. Publ. 260-2, Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards, October 1964. 35 cents.*

NBS Misc. Publ. 260-3, Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard, October 1964. 20 cents.*

NBS Misc. Publ. 260-4, Standard Reference Materials: Sources of Information on Standard Reference Materials, February 1965. In press.*

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ACCURACY OF SOLUTION X-RAY SPECTROMETRIC ANALYSIS OF COPPER-BASE ALLOYS

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X-ray fluorescence spectrometry has been investigated as an independent method for the analysis of certain major constituents in NBS standard reference materials. The determination of copper and zinc in cartridge and aluminum brass samples which were to be certified as standard materials, was selected for study. After a preliminary analysis, a solution of the unknown and a closely-matched synthetic standard were compared without the use of an internal standard or added control element. To achieve reliable results, close control of the type and concentration of acid was found necessary, and, for cells employing films as windows, the position of the film was critical. The temperature rise of the cell during irradiation was 0.1°C , which did not contribute significantly to error. Typical coefficients of variation obtained for individual results in a group of 8 runs were 0.3% for copper and 0.4% for zinc. The agreement between chemical and x-ray results was within 0.3% of the amount present for both elements.

1. INTRODUCTION

For certification of NBS standard reference materials of composition, it is desirable to employ at least two independent analytical methods to reduce the possibility of bias in the results. X-ray fluorescence spectrometry, with its inherent high precision, may serve as one of the methods providing that the factors affecting accuracy are evaluated.

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It is generally recognized that the ultimate in reliability is attained by the direct comparison of unknown with standard when they are uniform, identical in composition, and identically prepared [1]. In addition, both should be exposed to the excitation source in the same way. To approach these ideal conditions, it is necessary to determine and control the factors that are most critical in affecting accuracy.

Solutions were selected for this study because of the advantages that they offer. They are homogeneous, and after a preliminary analysis of the unknown, a synthetic standard closely approximating the composition of the unknown can be prepared. Moreover, differences in absorption and enhancement effects between unknown and standard can be reduced by dilution. In the comparison of solutions of an unknown with a synthetic standard, several factors may be expected to contribute to error:

1. When the solution cell includes a thin film, the films of the two cells may distend by different amounts thus changing the surface being irradiated.
2. The acid concentration may differ in the two cells, producing different absorption effects.
3. Temperature changes affect the density of the solutions.

By adding the same amount of a suitable control element to the solutions of synthetic standards and unknown and taking a ratio of the intensity of the analyte to the intensity of the control element, a partial compensation for the error is

differences in film position and acid concentration can be made. However, the selection of a suitable control element may be difficult because of possible precipitation or interference effects on other radiations to be measured. Therefore, to make this method more generally applicable a control element was not added. Our investigation was limited to the determination of copper and zinc by x-ray fluorescence spectrometry in the cartridge and aluminum brasses which were being analyzed for certification as NBS standard reference materials [2]. Data are reported on precision and accuracy and the principal factors affecting accuracy are discussed.

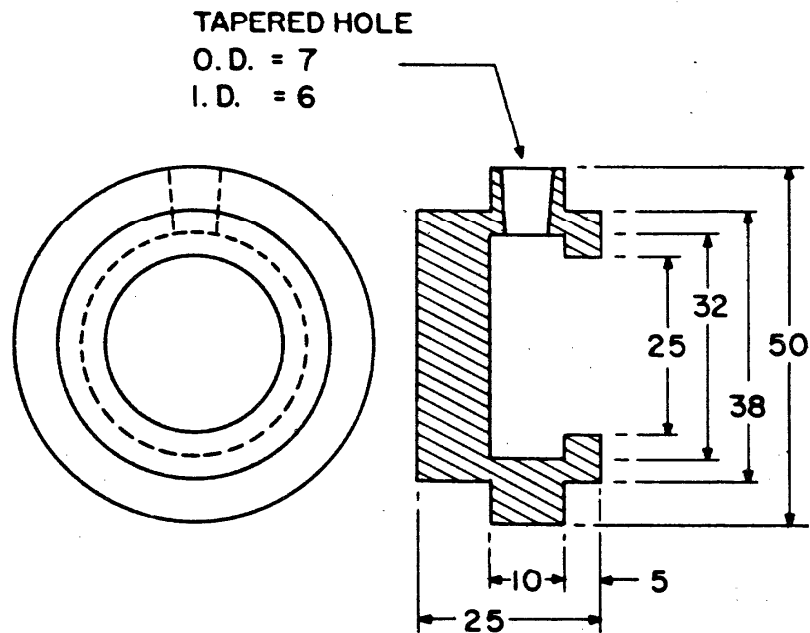
Previous work using x-ray fluorescence of solutions for the determination of copper includes the determination of that element in bronze heat-treating materials by Blank and Heller [3] who reported "a limit of error at the 95% confidence level" of approximately 1% expressed as a percentage of the mean value. Zinc was used as an internal standard. It was reported that no significant error was introduced in the chemical preparation. Bertin and Longobucco [4] determined copper, nickel, silver and gold in plating baths. Designed primarily as a rapid method, the agreement between chemical and x-ray methods was within 1 to 3 percent for all elements.

2. INSTRUMENTATION

A commercial, multichannel spectrometer of the curved crystal type was used for this investigation. Although the main features of the equipment were described previously [5],

additional information pertinent to this work is described below.

A horizontally-mounted x-ray tube having a platinum target and a 1.0 mm beryllium end window was operated at 50 kV and 35 mA to irradiate the solutions. The solutions were contained in cells of methyl methacrylate plastic having the dimensions indicated in Figure 1. After cementing a 0.0006-mm polyester



ALL DIMENSIONS IN mm

Figure 1. Diagram of solution cell.

(1/4 mil nominal Mylar) film with adhesive (Pliobond) [4] across the 25-mm opening, approximately 10 ml of solution was introduced into the cell and a tetrafluoroethylene polymer stopcock used as a closure. To minimize the possibility of

damage to the x-ray tube due to leakage, the spectrometer had been mounted on its side, thus placing the cell in front of, rather than above, the tube. This arrangement is possible since none of the components are dependent on gravity for operation.

The solution cell was irradiated by inserting it into the circular cavity of the sample holder, moving the holder horizontally approximately one-half meter into the spectrometer, alining the gear segments of the holder and x-ray tube shutter, and then twisting the holder to open the shutter. The sample holder serving also as a radiation shield during excitation, weighed almost 2 kg and was therefore awkward to move into position. To facilitate sample handling for irradiation, the holder was modified as shown in Figure 2, by attaching to the end of the holder a 25-mm diameter rod, 0.5 m long with a longitudinal keyway and by attaching to the side of the holder a roller bearing. Supported by a bracket attached to the side of the spectrometer, the sample holder assembly could be rolled into position with the keyway facilitating alinement of the gear segments. A hinged plate actuated by the sample holder assembly served as an additional safety shield.

While irradiating the sample through the Mylar film, element line intensities were integrated by capacitors connected to detectors. Details of spectrometer characteristics are given in Table 1. At the same time, a brass sample was also irradiated by the primary x-ray beam and the integrated,

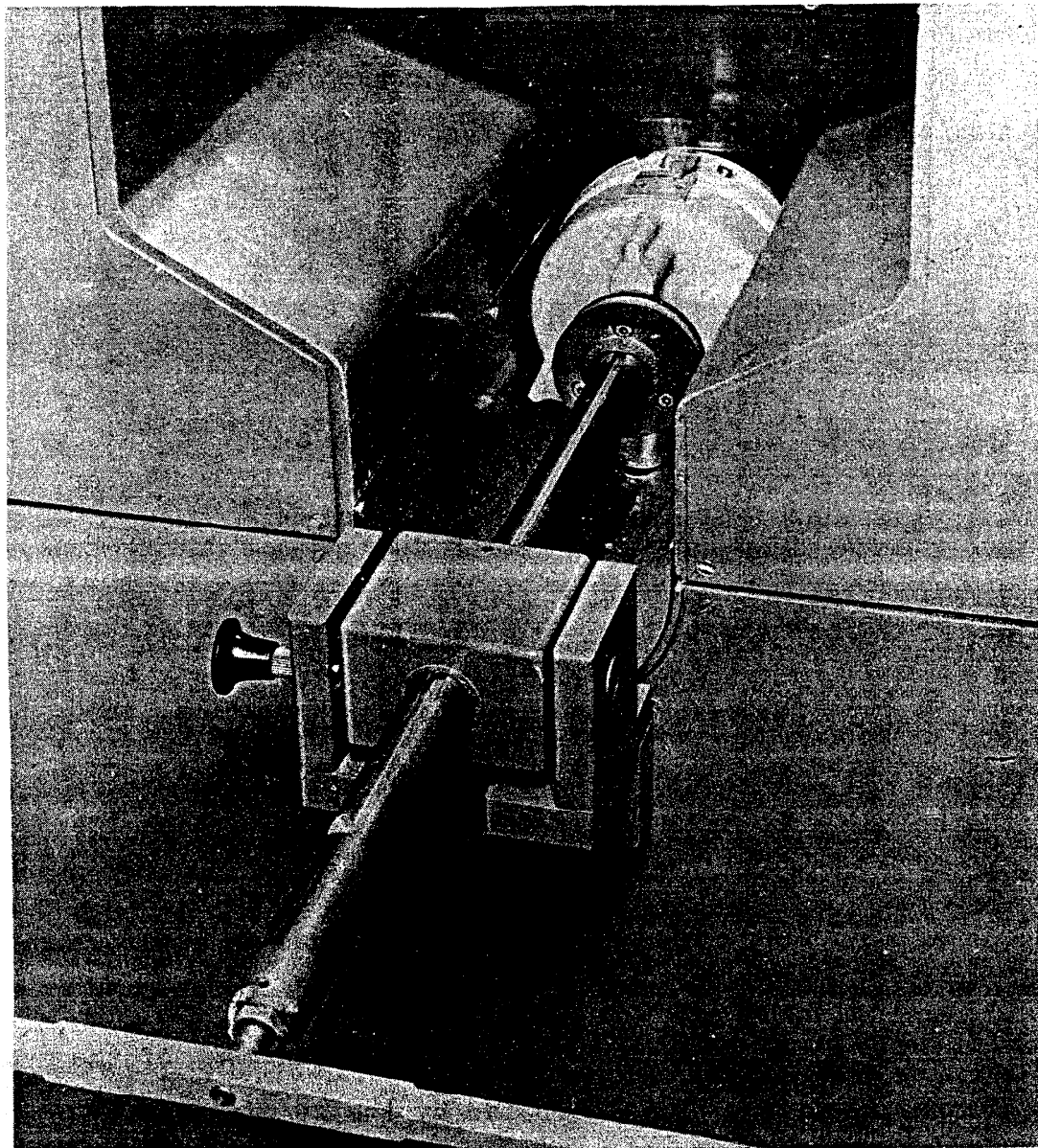


Figure 2. Sample-holder assembly of spectrometer.

non-dispersed radiation used to terminate the integration period of approximately two minutes. A digital voltmeter provided a measurement proportional to the voltage developed on each capacitor during the integration period. These numbers

Table 1. X-Ray Spectrometer Settings

Element	Wavelength Å	Crystal		Atmosphere	Detector
		Radius cm	Material		
Copper	K α 1.542	10 (4 in.)	LiF	Air	Proportional ^a
Zinc	K α 1.437	28 (11 in.)	LiF	Air	Proportional ^a

^aCounter measures average current for integration.

were displayed visually and were automatically typed on an electric typewriter. Linear analytical curves were developed for each element relating intensities expressed as digital voltmeter readings to the concentrations of the synthetic solutions for the range covered. The digital voltmeter response could be adjusted to read concentration directly. After a preliminary analysis of the unknown, another standard was then made up having this analysis and additional determinations were made.

3. EFFECT OF FILM POSITION

In the direct comparison method, cells containing solutions of the unknown and closely-matched standard are interchanged and ideally all conditions should remain constant except for the substitution of one solution for another. However, the hydrostatic pressure of the liquid distends the polymer film approximately 0.4 mm, an amount which may differ for each cell. To evaluate the magnitude of this effect on the results, the measuring system shown in Figure 3 was devised.

Three cells were used--two having tetrafluoroethylene polymer stopcocks, the other a plug of the same plastic.

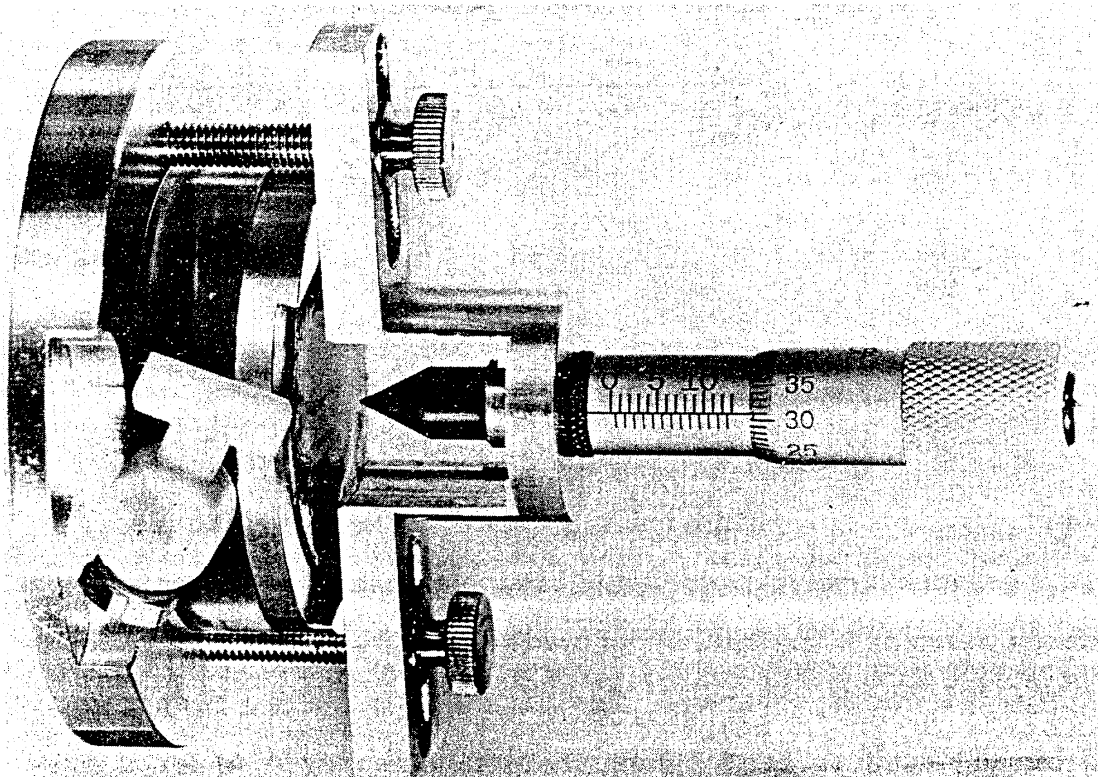


Figure 3. Apparatus to measure the position of the film.

Approximately 10 ml of a 1-Molar nitric acid solution of brass having a concentration of 10 mg of metal per ml was introduced into each cell. The position of the film could be changed by operating a small syringe attached temporarily to the stopcock, after which the stopcock was closed. The micrometer head, which could be read to 0.01 mm, had a pointed sleeve of black plastic to facilitate observing the position of contact. Placing the cell on edge, in the position that it would normally be irradiated, a reading was taken at the surface of the cell to which the film had been cemented and a second reading taken at the center of the film--the difference being a measure of the amount

of bowing. Intensity readings were taken for each position of the film surface, after which the film position was again checked. No change in film position was observed. Intensity readings taken of the two cells with stopcocks were alternated with those of the cell with a plug. Since the film position of the latter remained constant, it served as a reference cell to correct for instrumental drift that might occur.

Figures 4 and 5 show the effect of changing the position of the film surface on the intensity of the $K\alpha$ radiations of zinc and copper respectively. The film is distended by hydrostatic pressure approximately 0.4 mm and bowing the film an additional 0.10 mm from this position causes the zinc $K\alpha$ intensity to increase by 0.19%. For a solution having a zinc concentration of 30.30% by weight based on metal content, a value of 30.36% would be obtained. For copper, a 0.10 mm change in film position produces a 0.069% change in intensity and a copper value of 79.35%, by weight based on metal content, instead of 79.30%.

4. EFFECT OF ACID CONCENTRATION

To determine the effect on intensity of a difference in acid concentration between solutions of unknown and standard, intensities were measured for solutions having different acid concentrations. Three nitric acid solutions of NBS C1120 were prepared, each containing the same concentration of brass, 10 mg per ml. The excess nitric acid was removed by evaporating the solution to dryness on a steam bath, adding

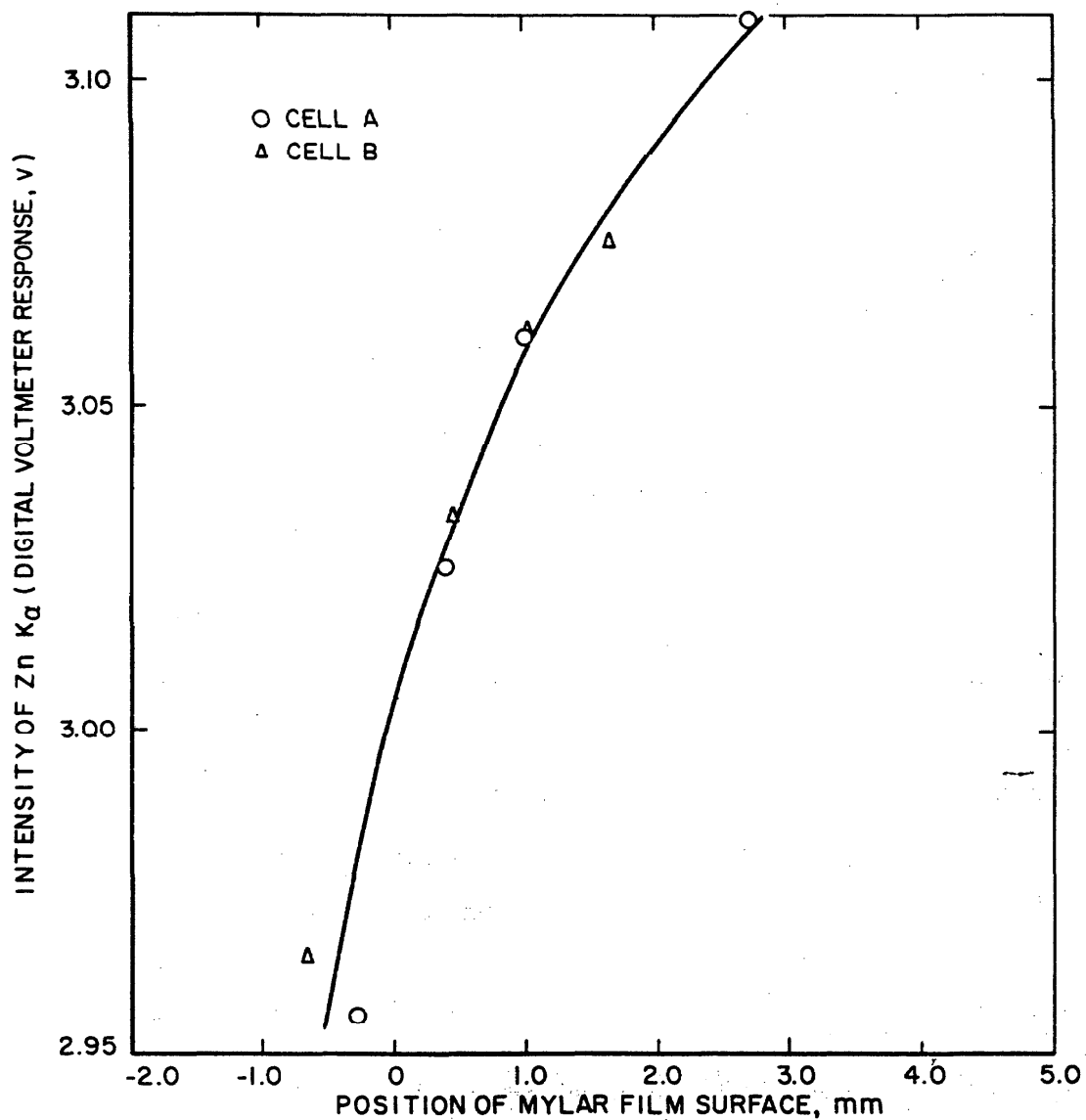


Figure 4. Effect of changes in film position on zinc K α intensity.

water, re-evaporating the solution to dryness and repeating this procedure. Nitric acid was pipetted to each solution to obtain concentrations of 0.64, 1.3 and 3.2 Molar. The

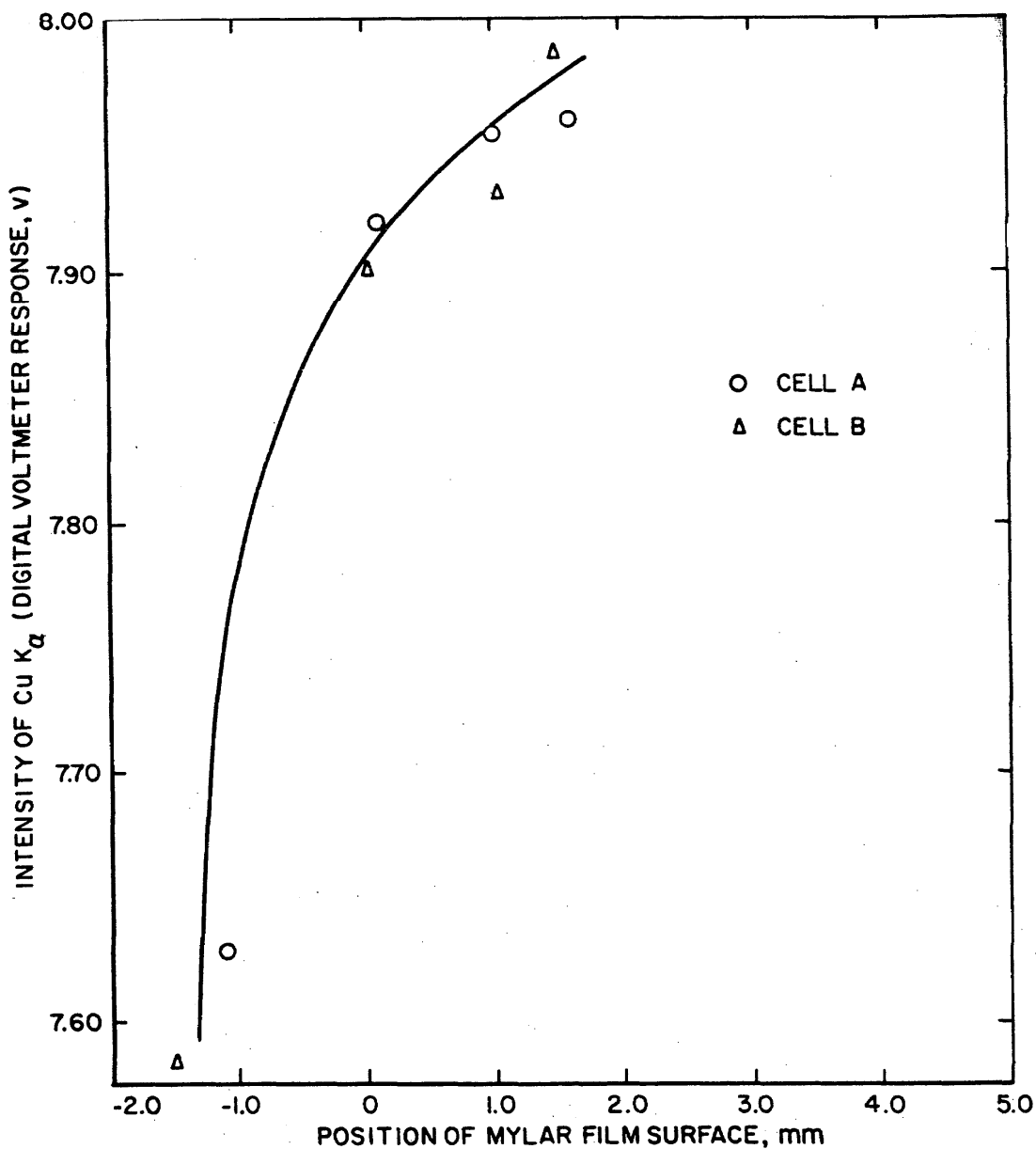


Figure 5. Effect of changes in film position on copper K α intensity.

intensities of the fluorescent radiations were measured and graphs made relating intensities to concentrations of acid. Figures 6 and 7 show the effect of a change in the nitric

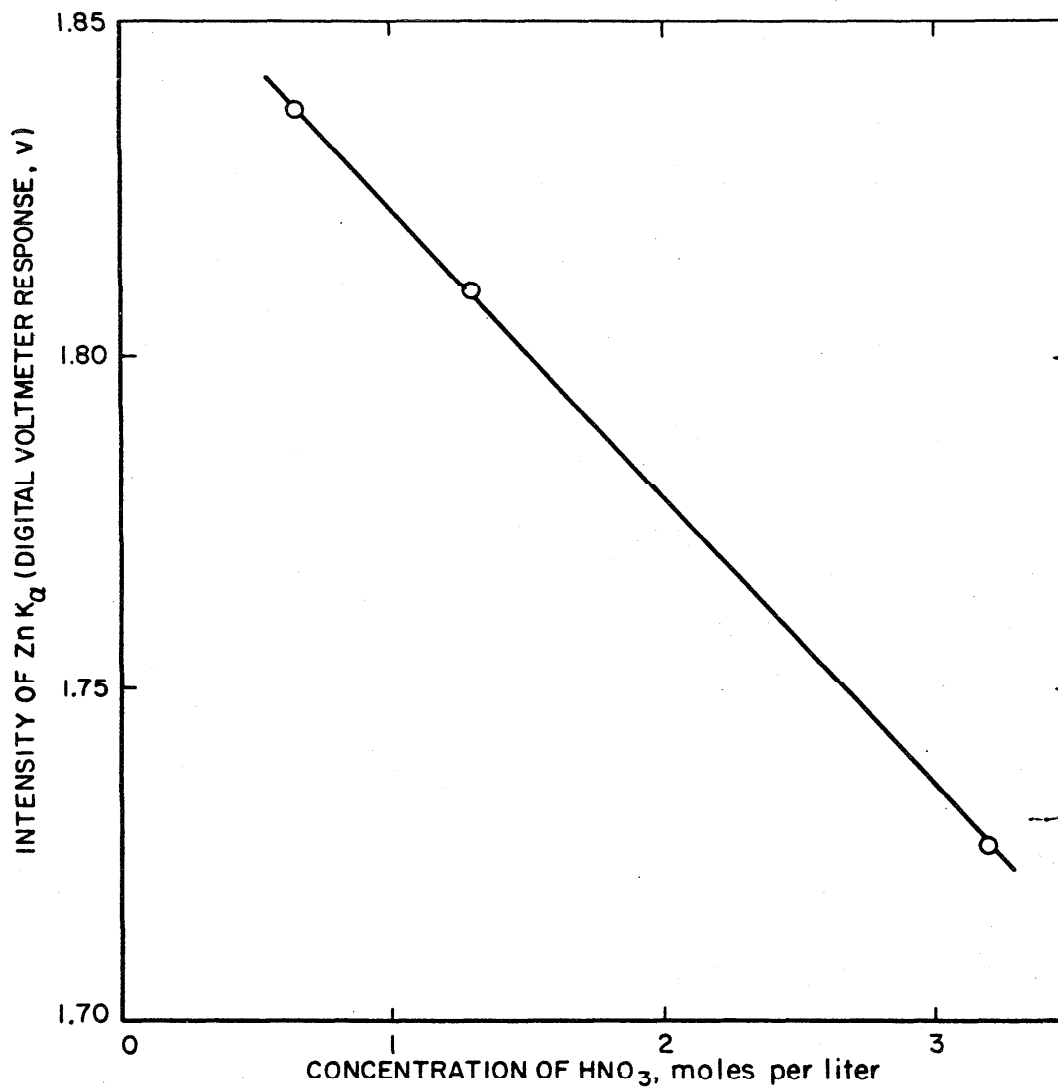


Figure 6. Effect of changes in nitric acid concentration on zinc $K\alpha$ intensity.

acid concentration on the $K\alpha$ radiations of zinc and copper respectively. Adding 1.6 millimoles of nitric acid to 10 ml of the brass solution, which was 1 Molar with respect to nitric acid, resulted in a 0.38% decrease in zinc intensity. This was

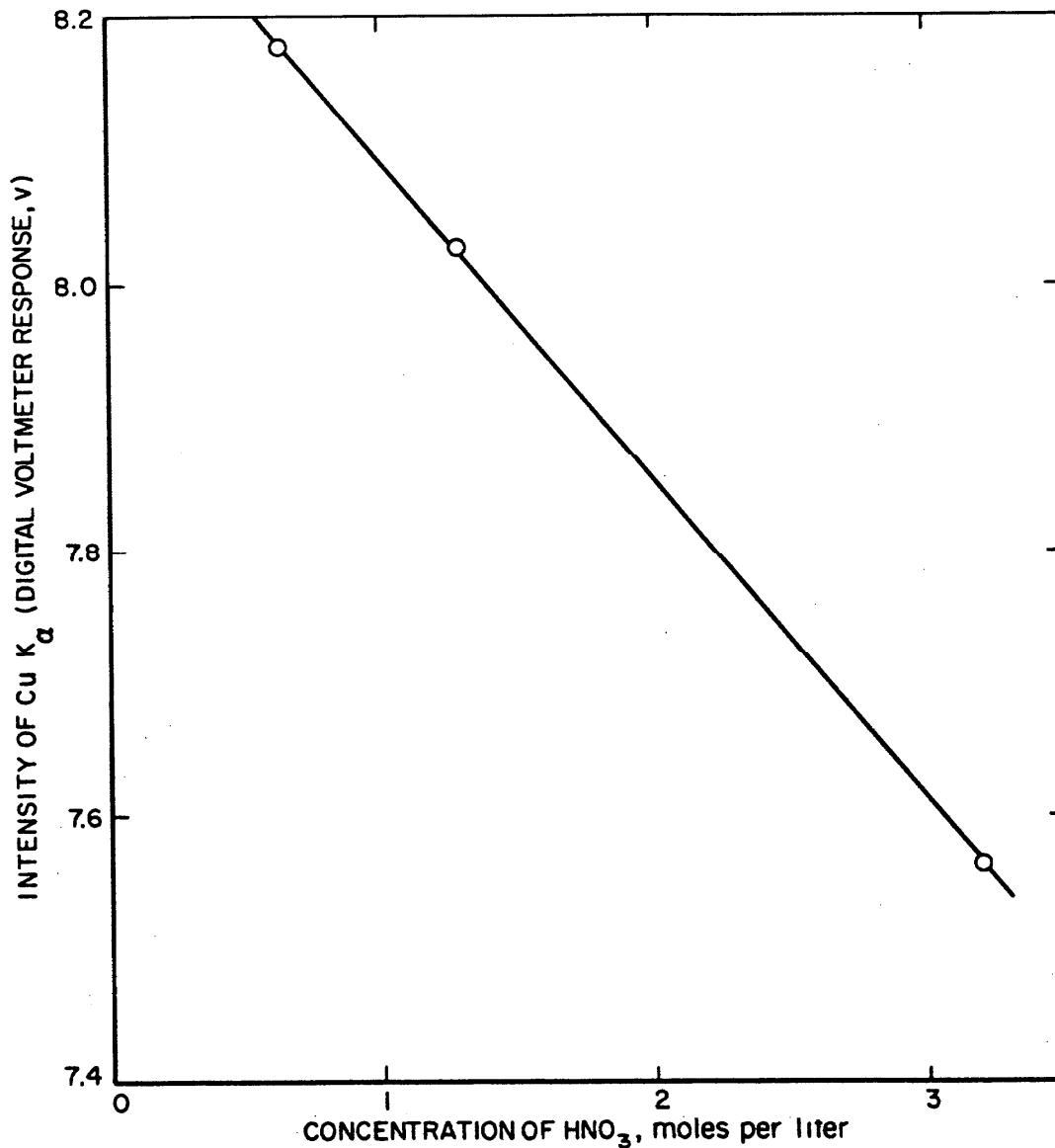


Figure 7. Effect of changes in nitric acid concentration on Copper K α intensity.

equivalent to adding 0.1 ml of 70% nitric acid to the cell volume which would have resulted in a zinc value of 18.05% by weight instead of the actual concentration of 18.12%. For copper, the same increase in nitric acid concentration resulted in a 0.48% decrease in intensity and therefore a copper value

of 79.89% by weight would have been obtained instead of the actual concentration of 80.29%.

5. EFFECT OF TEMPERATURE

The temperature rise occurring in a cell during the two minute irradiation period was measured with a calibrated thermistor placed inside the cell so as to avoid the primary x-ray beam. A change of resistance equivalent to a temperature rise of 0.1°C was obtained. The resulting small change in density of the solution would not produce a significant change in the intensity measurements.

6. APPLICATION TO ANALYSIS

Since close control of acid and film position was found to be necessary for accurate results, the following procedure was used. A 500-mg sample of brass was dissolved in 10 ml of water and 4 ml of concentrated nitric acid. To remove excess nitric acid, the solution was evaporated to dryness on a steam bath, several ml of water added to the residue, evaporated to dryness again and the procedure repeated. A portion of 20 ml of a nitric acid solution composed of one volume concentrated nitric acid plus four volumes of water was pipetted to dissolve the residue. The solution was transferred to a 50-ml volumetric flask and made to volume with water at 20.0°C . The same procedure was used to prepare synthetic standard solutions from metals having 99.99% purity.

Solution cells were filled with solutions of synthetic standards and unknown and, after a preliminary analysis of the unknown from a graph relating intensity to concentration, another synthetic standard was prepared having this analyzed composition. After introducing the new standard into a cell, the position of the film was measured by means of the system shown in Figure 3 and then adjusted to the same position as that of the cell containing the unknown. These two solutions were then intercompared to obtain the final concentration of the unknown. After the solutions were prepared it was relatively easy to make multiple runs on the x-ray spectrometer.

This procedure was applied to the determination of copper and zinc in several brass NBS standard reference materials. The x-ray results and measure of their precision are compared with the provisional chemical values [2] in Table 2. In this table, a run is a concentration value derived from an intensity measurement with the cell having been removed and reinserted into the sample holder between each measurement.

Aluminum was not determined because its soft radiation is absorbed to a large extent by the film resulting in poor sensitivity and precision.

7. DISCUSSION

The coefficient of variation for an individual run in a group of eight was found to lie between 0.17 to 0.46%, the precision of the method being limited mainly by instrumental instability. By taking the mean of eight runs the effect of drift

Table 2. Comparison of Chemical and X-Ray Results.

NBS Sample Number	Element	Chemical Results ^a	X-Ray Results ^b	Standard Deviation of the Mean ^c	Coefficient of Variation of the Mean ^d
		%	%		
C1100	Cu	67.4 ₃	67.3 ₃	0.07	0.10
	Zn	32.2 ₀	32.2 ₅	0.03	.09
C1101	Cu	69.5 ₀	69.6 ₀	0.07	.10
	Zn	30.3 ₄	30.2 ₈	0.04	.12
C1102	Cu	72.8 ₅	72.8 ₆	0.06	.08
	Zn	27.1 ₀	27.0 ₆	0.03	.12
C1118	Cu	75.0 ₇	75.0 ₆	0.09	.12
	Zn	21.9 ₁	21.9 ₇	0.04	.16
C1119	Cu	77.1 ₂	77.2 ₉	0.05	.07
	Zn	20.5 ₃	20.4 ₉	0.03	.15
C1120	Cu	80.1 ₄	80.2 ₉	0.05	.06
	Zn	18.1 ₀	18.1 ₂	0.02	.12

^aAverage reported on provisional certificate.

^bMean of 8 runs.

^cStandard deviation of the mean $\bar{s} = \sqrt{\frac{d^2}{n(n-1)}}$, where d is the difference of the determination from the mean, and n is the number of runs.

^dCoefficient of variation of the mean, C.V. = $\frac{100 \bar{s}}{C}$ where C is the average concentration in percent.

was partially corrected. However, the drift was irregular and could not be entirely compensated for. Improvement in the x-ray method should lie in the direction of better control of drift.

Since the accuracy of the method depends on closely matching the composition of solutions of samples and synthetic standards, a preliminary examination of the sample should be made.

It is necessary to note particularly the presence of elements having principal x-ray radiations lying several tenths of an Angstrom below the absorption edge of the analytical line of the analyte and also those elements which have large mass absorption coefficients at the wavelength of the analytical line. The preparation of synthetic standards should include these elements at approximately the same concentration as in the sample.

Significant distention of the thin film cover on the sample cell was observed when so mounted that the film was vertical. This indicates the necessity for determining and adjusting the film position to the same relative position for both sample and synthetic standards.

The same acids must be used to prepare the synthetics as were used to dissolve the samples and the final acid concentration should be the same for both standard and samples.

It is of interest to compare the x-ray method with chemical methods for the determinations made. Copper can be determined by electrodeposition with a coefficient of variation of 0.01 to 0.02% and interferences are not serious. This represents one of the simplest and most accurate chemical procedures and is preferred for the determination of major amounts of copper.

Because of difficulty in the chemical determination of zinc, even high concentrations are often reported "by difference." However, zinc can be determined with a coefficient of variation of 0.1 to 0.2% by a double precipitation with hydrogen sulfide

followed by ignition to the oxide. Here the x-ray method is more competitive, especially for lower concentrations of zinc.

The differences between results by the chemical and x-ray methods lay between 0.02 and 0.10% except for zinc in Cl1118 where it was 0.17%.

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