Mass Spectrographic Determination of Impurities in Liquids

JUNJIRO KAI* and MASAYO WATANABE*

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Abstract:

Spark source mass spectroscopy is applied to determine impurities in a drop of liquid sample. The water drop evaporation technique and electroplating technique are investigated combined with internal standard technique. Some methods of calibration has been examined. It is shown that in many cases the impurities in a liquid sample may be determined with relative deviation of $\pm 10\%$ provided the internal standard is used. The impurity enrichment on surface has been revealed to occur in electroplating, which results the higher sensitivity compared with water drop evaporation technique. The absolute sensitivity for determination of impurity amounts to about 10^{-4} μg of iron.

I. Introduction

Spark source mass spectroscopic techniques have been used widely in recent years in the analysis and investigation of solids^{1),2)}.

The radio frequency spark is capable of sampling a wide variety of materials—metals, ~~semiconductors~~ and insulators in the form of solids or powders.

Two methods were devised for the analysis of liquid samples. In one method, ³⁾⁴⁾ impurities in a liquid were detected by contaminating an otherwise clean surface of suitably pure material with the liquid, and sparking directly to the contaminant residue on the surface. In the second method, a liquid was mixed with a suitably high grade powder to form a paste, which was frozen⁵⁾ to be supported as an electrode or dried and pressed^{6),7)} into an electrode.

Methods for analyzing liquids are applicable not only to samples that are initially solutions, but also to samples that can be made into solutions. Moreover, the methods have the advantage that absolute standards may be prepared by chemical means.

In this investigation, first method was used combined with an internal standard

technique, and some methods of calibration are examined to determine metallic impurities in a drop of pure water. Evaporation technique of water drop developed by Ahearn was used and electroplating technique suitable for such a drop was developed.

II. Experiments and Results

2.1 Water Drop Evaporation Technique

2.1.1 Preparation of sample electrodes.

Standard deionized water samples doped simultaneously with salts of manganese, iron, copper, zinc, and silver were prepared. The concentrations of these impurities ranged from 10 ppb to 160 ppm in atomic fraction.

The liquid evaporation technique developed by Ahern was used as schematically shown in Fig. 2.1. A drop of water was hanged from the flared tip of the electrode and evaporated with a infrared lamp. The volume of one drop of water, about 3 mm in diameter, was

*Central Research Laboratory, Mitsubishi Electric Corp.
(80 Nakano, Minami Shimizu, Amagasaki, Japan)

Fig. 2.1 Water drop evaporation technique
a: sample electrode b: water drop

estimated to be about 0.016 cc. The electric field, which was increased as evaporation proceeded, pulled down the drop and prevented it from creeping up along the side of the electrode. The sample electrode and the pointed counter electrode were machined from a copper rod (five nines, Mitsubishi Metal Mining Co., Ltd., Tokyo, Japan) or a graphite rod (Ultra Purity grade, Ultra Carbon Corp., U.S.A.). Graphite rod was machined with cutting tool made from a piece of ceramic plate and presparked on the tip surface to avoid metallic contamination. Copper rod was machined with usual cutting tool made of steel and etched in nitric acid and hydrochloric acid.

2.1.2 Apparatus and operating conditions.

A mass spectrograph of Mattauch-Herzog type provided with a radio frequency spark source developed in our laboratory was used for the experiments. The mean radius of the electrostatic energy selector of this spectrograph is 150 mm, and the mass range from M to $16 M$ is covered in a single exposure on a photographic plate.

Fig. 2.2 Electrode pair mounted in ion source.
a: sample electrode
b: counter electrode
c: accelerating electrode

The electrode pair was mounted in the ion source as shown in Fig. 2.2, and a pulsed 4MHz frequency voltage of about 20KV amplitude was applied. The pulse had a duration of 300 μ s and was repeated with a rate of 60 pps. During the sparking, the pointed counter electrode was fixed and the sample electrode was moved to be scanned on the entire surface of the tip with spark, so that the position of the spark in the ion source was kept stationary.

Ions were accelerated by a potential difference of 13.6 kV.

Seven exposures were made for each sample with the same exposure of 3.5×10^{-10} coulombs. Ilford Q2 plates were used and developed with ID-19 developer at 20°C for 3.5 minutes.

2.1.3 Results.

The spectral line densities were measured by microphotometer and three types of calibration curves were examined using the data of first exposure on each plate.

(1) Density ratio vs concentration ratio

In the first type of calibration curve, the ratio of appointed isotopic spectral line density of element to be determined to that of internal standard is plotted against the ratio of concentration of the element to be determined to that of the internal standard. The concentration of the internal stand-

ard is kept constant.

Fig. 2.3 shows the calibration curve for iron with the internal standard of zinc of 4 ppm in atomic fraction. Copper electrodes were used in this experiment. Zinc has five

isotopes and iron has four isotopes. All the combinations of available isotopic spectral lines of zinc and iron are used in plotting Fig. 2.3.

Fig.2.3 Calibration curves (1) for iron.

The concentration of zinc in the samples which had the ratio C_{Fe}/C_{Zn} of 0.5, 2, and 3 were really not 4 ppm, but 44, 33 and 5.4 ppm respectively, whereas the points for these samples seem to fall on a curve together with other samples of zinc concentration of 4 ppm. It is felt from the fact that the density ratio depends only on the concentration ratio and does not depend on the absolute concentration.

(2) Density ratio vs [(concentration) x (isotopic abundance)]ratio.

We have already shown the advantage of the use of available isotope distribution in

preparing the calibration curve of the element. 8),9) It is shown that under five assumptions the number of ions fall on unit area of a isotopic spectral line is proportional to the product of the concentration of the element and the isotopic abundance. In this second method, the density ratio is plotted against the ratio of [(concentration C) x (isotopic abundance r)] of the element to be determined to that of the internal standard.

Fig. 2.4 shows the calibration curve for iron with the internal standard of zinc.

The calibration curve corresponding to density ratio vs concentration ratio type is

Fig. 2.4 Calibration curve (2) for iron.

shown also in dashed line in Fig. 2.4. The fair agreement of the curves in Fig. 2.4 indi-

cates that when the element to be determined and/or the internal standard have

Fig. 2.5 Calibration curves (2) for manganese, copper, zinc, and silver.

appropriate isotope distribution, calibration curve may be prepared using only one standard sample. This may be confirmed from the results shown in Fig. 2.5, in which the calibration curves of manganese, copper, zinc, and silver with the internal standard of iron of 20 ppm are shown. Graphite electrodes were used in this case.

(3) Ion intensity ratio vs concentration ratio

To avoid the effect of variation of the characteristics from plate to plate, the ion intensity ratio may be used instead of line density ratio in preparing a calibration curve.

Fig.2.6 Characteristic curve for a plate.

The characteristic curve of photographic plate is prepared from spectral lines of an element which has suitable isotope distribution. The line densities in one exposure are plotted against the isotopic abundance in logarithmic scale. An example of such a characteristic curve is shown in Fig. 2.6, and the ion intensity ratio I_M/I_I of an element M to internal standard I is given by next equation,

$$\frac{I_M}{I_I} = \frac{E_M}{r_M} \cdot \frac{r_I}{E_I} \quad \dots (2.1)$$

where, E_M and E_I are read from Fig. 2.6 corresponding their line densities D_M and D_I .

Fig. 2.7 shows calibration curves for manganese, copper, zinc, and silver using the same data shown in Fig. 2.5.

Fig.2.7 Calibration curves (3) for manganese, copper, zinc, and silver.

2.2 Electroplating Technique

An electroplating technique for preparing the sample electrode in the analysis of liquid samples has been demonstrated by Ahearn. 3),4)

We have developed an electroplating technique suitable for a drop of water, which will be described here compared with water drop evaporation technique.

Standard deionized water samples doped simultaneously with manganese, iron, and zinc were prepared. The concentrations of these impurities ranged from 25 ppb to 10 ppm in atomic fraction. Iron was doped as internal standard and its concentration was 5 ppm for all the samples.

The electroplating technique developed here is shown schematically in Fig. 2.8.

Electrodes of copper or graphite shaped in the same way as described in paragraph

Fig.2.8 Electroplating technique.

- a: sample electrode
- b: sample liquid
- c: gold plate

2.2.1 were used and held in a pin vise fixed on a vertical adjustment mechanism. A drop of sample whose volume had been measured and controlled by a micropipette as 0.008 cc was fallen on a rigorously cleaned gold plate

of four nines purity. Then the electrode was lowered till the surface of the tip touched the liquid. The gap between the tip and the gold plate was about 1.5 mm. Potential difference of about 18 V was applied between the gold plate and the sample electrode, the latter being on the cathode side. About 10 mA of electrolytic current passed at first and decreased to 2 mA for a few minutes, then the electrode tip surface was lowered to reduce the gap to about 1 mm. After 10 minutes the sample electrode was raised and next 0.008 cc drop of the sample was measured and fallen on the gold plate. Thus the sample volume of 0.016 cc

was used for each sample to compare the results clearly with that of water drop evaporation technique described in section 2.1.

2.2.2 Results.

The electrode pair was mounted in the ion source in the same way as shown in Fig. 2.2, and experiments were performed under the same conditions as in the case with water drop evaporation technique.

Ion intensity ratios were plotted against concentration ratios as shown in Fig. 2.9.

Fig.2.9 Calibration curves for manganese, and zinc.
Cu: copper electrode ∇ : graphite electrode

III. Discussion

Fig. 2.7 and 2.9 shows that in many cases the impurities in a liquid may be determined with relative deviation of $\pm 10\%$ provided the internal standard is used. This

accuracy is better than that reported for impurity determination in bulk metal, 2), 8) and the advantage of preparing standards by chemical means is evident.

Fig.3.1 Variation of line intensity in successive exposures, water drop evaporation technique.
a: copper electrode b: graphite electrode

Table 3.1 shows the lower limits for impurity determination in a drop of water of 0.016 cc by the two techniques described here.

2.2.1 Preparation of samples electrodes

The electroplating technique is more sensitive than water drop evaporation technique, and the copper electrode gives better results than graphite electrode in sensitivity.

The reason of these results was searched for in the variation of line intensity in successive exposures. Fig. 3.1 shows the variation of line intensity in the case in

which the water drop evaporation technique has been used. In this case, graphite electrode has shown slower decrease in line intensity than copper electrode, which implies the relatively deep penetration of impurities into the graphite electrode body remaining less impurities on the surface, and resulting the less sensitivity at the first exposure. Fig. 3.2 shows the variation of line intensity in the case in which electroplating technique has been used. In this case, nearly equal rate of decrease of line intensity is

Table 3.1 Lower limits for impurity determination in a drop of water, ppb in atomic fraction.

Electrode	Sample electrode technique	
	Electroplating	Water drop evaporation
Copper	2 - 5	7 - 25
Graphite	3 - 10	40 - 500

Liquid volume : 0.016 cc

1ppb = $5 \times 10^{-5} \mu\text{g Fe}$

Fig.3.2 Variation of line intensity in successive exposures, electroplating technique.

a: copper electrode b: graphite electrode

shown in both the electrodes. The rate seems to be slightly rapid than copper electrode in Fig. 3.1. This implies enrichment of impurities on surface by electroplating and may explain the higher sensitivity of electroplating technique compared with water

drop evaporation technique.

The absolute sensitivity of this spark source mass spectrograph for determination of impurity may amount to about 10^{-4} μg of iron as estimated from Table 3.1.

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