

## SHORT COMMUNICATIONS

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### Rapid iodometric determination of copper in some copper-base alloys

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IN recent years a mixture of hydrofluoric and nitric acids has occasionally been used for the dissolution of alloys. Thus, Garate and Garate<sup>1</sup> have described the dissolution of friction alloys, containing tin, antimony and lead, in such a mixture before the determination of the alloying constituents. The present authors found<sup>2</sup> that alloys of bismuth, tin, lead and cadmium are also readily dissolved in this mixture of acids.

Dozin<sup>3</sup> noted that copper-tin alloys may be dissolved in a mixture of hydrofluoric and nitric acids, but no detailed directions could be found in the literature by the present authors on the dissolution procedure or on the possibility of applying conventional means of completing the analysis of such alloys. It seemed useful to investigate this analysis of copper-tin alloys further; conventional procedures are laborious because copper is adsorbed on the precipitate of hydrated tin(IV) oxide formed during dissolution of the alloys in nitric acid alone.

According to the British<sup>4</sup> and American<sup>5</sup> standard procedures, in which the copper is eventually determined electrolytically, tin should first be removed by volatilisation as tin(IV) bromide if more than 1-1.5% of this element is present. A similar procedure is recommended in the more or less official German standard.<sup>6</sup>

Kühnel-Hagen and Salomonson<sup>7</sup> claim that good results are obtained by iodometric titration of copper in its alloys after dissolution in nitric acid alone and digestion for 10-30 min. In their procedure up to 20% of tin apparently gives no error, but much lead should not be present. Orlik and Tietze<sup>8</sup> dissolve copper-base alloys in a mixture of nitric and sulphuric acids, evaporate until crystals of copper sulphate appear and eventually titrate the copper iodometrically. From their paper it is not clear how much tin may be present.

The iodometric finish was also employed in our investigations. Bromine was used to oxidise arsenic and antimony to the quinquivalent form, when both metals may be masked by fluoride if one works at a suitable pH.<sup>9</sup> Iron(III) may also be masked with fluoride.

## EXPERIMENTAL

### General

The solvent mixture is prepared by mixing 3 volumes of 40% hydrofluoric acid, 14 volumes of 65% nitric acid and 5 volumes of water. In a first series of experiments, polypropylene beakers were heated in a water-bath because it was feared that the solvent attack on glass might be disadvantageous in analysis. In later experiments it was, however, found that Pyrex vessels could be used if they were heated gently during the dissolution procedure. If the vessels are heated too vigorously an insoluble compound is formed and erroneous results are obtained.

With the final procedure, in each experiment the vessels lost only about 150 mg of their weight. This proved to have no unfavourable effect on the results. The standard deviation was even decreased compared with results obtained when polypropylene beakers were used, possibly because the excess of bromine and the nitric oxides are expelled more completely at the temperature used in the Pyrex vessels.

In all experiments described below 150-ml Pyrex Erlenmeyer flasks were used, covered with a polypropylene watch-glass during heating. The vessels were heated gently on an electric hot-plate. The power-supply was regulated to bring the content of the vessels just to, or slightly below its boiling point. The time required for dissolution did not exceed 2 min in all experiments described below. In one experiment the influence of the presence of much lead was investigated, because lead fluoride is slightly soluble. An (slightly inhomogeneous) alloy, containing about 30% of lead and 5% of tin, was attacked in the way described below and this alloy, was dissolved in about 5 min.

*Procedure*

Weigh exactly a quantity of alloy, containing about 200 mg of copper, in a 150-ml Pyrex Erlenmeyer flask, add 5 ml of solvent mixture, cover the vessel with a polypropylene watch-glass and heat it gently. After dissolution add saturated bromine solution until a distinctly brown colour is seen. Continue heating for 5 min, add about 200 mg of urea, then heat 1 min more. Cool to room temperature, add 25 ml of water, 25 ml of 20% ammonium acetate solution (giving a pH of about 4), 1 ml of 40% hydrofluoric acid and 3 g of potassium iodide. Titrate with 0.1M sodium thiosulphate solution. Add starch solution just before the end-point, titrate further until the colour bleaches, then add 2 g of ammonium thiocyanate and finish the titration. Standardise the sodium thiosulphate solution against electrolytic copper, using the same procedure.

## RESULTS AND DISCUSSION

The procedure was checked with four standard samples and with some mixtures of electrolytic copper with pure tin or antimony. Results are given in Table I. The results show a standard deviation of about 0.1%, and the systematic error seems well below this value.

TABLE I.—ANALYSIS OF COPPER-BASE ALLOYS AND "SYNTHETIC" MIXTURES AFTER DISSOLUTION IN A MIXTURE OF HYDROFLUORIC AND NITRIC ACIDS

Expt.	Sample	Copper content, % (certificate value)	Other important constituents, %	Copper found, %	Error, %
1	NBS 52 c	89.25	Sn 8	89.37; 89.13; 89.42	+0.1; -0.1; +0.2
2	BCS 207/1	88.1	Sn 10; Sb 0.1; As 0.1	88.15; 88.09; 88.14	+0.1; 0.0; 0.0
3	BCS 183/1	84.8	Sn 5; Sb 0.2; As 0.1 Pb 4; P 0.5	84.87; 85.00; 84.80	+0.1; +0.2; 0.0
4	NBS 63	78.05	Sn 10; Sb 0.5; As 0.2 Pb 10; P 0.6	78.02; 78.07; 77.97	0.0; 0.0; -0.1
5	Electrolytic copper	ca. 200 mg	ca. 100 mg of tin added	recovery 99.96; 99.92; 99.88; 99.90	0.0; -0.1; -0.1
6	Electrolytic copper	ca. 200 mg	ca. 10 mg of antimony added	recovery 99.82; 99.98	-0.2; 0.0

Similar experiments were carried out in which a mixture of 3 ml of 65% nitric acid and 2 ml of water was used as solvent, and 2 ml of 40% hydrofluoric acid were used after ammonium acetate was added. The thiosulphate used here, was standardised after dissolution of copper in nitric acid alone. When duplicating experiments 1, 2, 3 and 6 (Table I) with this modification, the results seemed as good as when a mixture of hydrofluoric and nitric acid was employed. Standard NBS 63 dissolved, however, with great difficulty and the results were 0.5%, 0.3% and 0.2% low; also, if 30–35% of tin was added (similar to experiment 5) the results were 0.2%, 0.7%, 1.1% and 0.9% low.

It should be pointed out that some difference is possible in the results obtained with alloys, when compared with results obtained with "synthetic" mixtures of the same composition. It seems probable, however, that this difference may be neglected in cases where the sample is completely dissolved. It may be expected, therefore, that alloys containing up to 35% of tin or up to 5% of antimony (and possibly more of these elements) will give good results when dissolved in a mixture of hydrofluoric and nitric acids. In cases when nitric acid alone is used as a solvent, residues are left and the amount of copper adsorbed may be different for alloys and mixtures. It cannot be assumed, however, that this amount may be neglected if much tin is present in an alloy. A final conclusion, therefore, may be that the use of a hydrofluoric-nitric acid solvent mixture gives good results in many cases where the use of nitric acid alone cannot be recommended.

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**Summary**—Copper-base alloys, especially those containing tin, are readily dissolved in a mixture of hydrofluoric and nitric acids. In the resulting solution copper can be titrated iodometrically in the conventional manner.

**Zusammenfassung**—Legierungen auf Kupferbasis, besonders zinnhaltige, lösen sich leicht in einer Flußsäure-Salpetersäure-Mischung. In der erhaltenen Lösung kann Kupfer in üblicher Weise jodometrisch titriert werden.

**Résumé**—Les alliages à base de cuivre, spécialement ceux contenant de l'étain, se dissolvent aisément dans un mélange d'acides fluorhydrique et nitrique. Dans la solution résultante, on peut doser le cuivre de façon usuelle par iodométrie.

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### A simplified sampling technique for use with the Weisz ring oven: Application to qualitative analysis of some gold and silver alloys

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#### INTRODUCTION

APPLICATIONS of the ring oven technique have been described for microchemical qualitative and semiquantitative analysis of several types of alloy.<sup>1-3</sup> Separation schemes and identification reactions specially designed for ring oven work have also been published.<sup>4,5</sup> Nevertheless, detailed procedures of analysis are still missing for certain alloys.

Apart from direct chemical attack on the specimen, two main types of sampling procedure have so far been suggested. One method, proposed by Stephen,<sup>2</sup> depends on electrolytic dissolution of the sample in combination with ring oven technique and was applied to the analysis of several non-ferrous alloys. Nall and Scholey<sup>3</sup> used the same procedure but for the sampling of steel. As far as electrolytic sampling is concerned, no positive evidence has so far been presented as to whether the composition of the dissolved sample is strictly equivalent to that of the original specimen. Where figures of a more quantitative nature are desired, there would be a definite risk of biased results, because the normal potential values of the constituents cover a wide range.

The second method of sampling is based on mechanical abrasion, as described by Strebing and Holzer,<sup>6</sup> who rubbed the specimen with a microscope slide having a circular roughened section, and that mentioned by Ballczo<sup>7</sup> who applied a 2-mm corund stick in the manner of a file. These two procedures suffer from the disadvantage that only convex or protruding parts of the specimen can be sampled.

The present authors have overcome the disadvantages of the above sampling procedures by introducing a simplified technique of mechanical abrasion for sampling some gold and silver alloys. This was achieved by using a 4-mm Pyrex glass rod with a hemispherical tip which was ground on a carborundum disc to provide a rough surface of about 25 mm<sup>2</sup>. Up to 100 µg of sample can be obtained by rubbing the tip under gentle pressure, rotating it against the sample and also tilting it at various angles, until most of the rough surface is coated with abraded material. In this way it is possible to obtain a sample from almost any part of a specimen, including concave or curved surfaces, inner surfaces of vessels or other parts of special interest, such as welded seams.