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Note

Determination of traces of copper and aluminium in zinc by gas chromatography with the microwave plasma detector

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The usefulness of a microwave plasma detector¹ in the gas chromatography of volatile metal chelates has been demonstrated by us^{2,3} and by other workers⁴. This detector is highly sensitive and selective, and has been successfully applied to the determination of beryllium, aluminium and chromium (as acetylacetonates and as trifluoroacetylacetonates) and of, *e.g.*, scandium, iron and copper as trifluoroacetylacetonates. However, its application to the analysis of metal samples for impurities present at the low ppm level has not been reported. This paper describes the determination of traces of copper and aluminium in zinc metal by using this detector. The trace elements were extracted into trifluoroacetylacetone (TFA)-chloroform from the sample solution at pH 4.5, and the organic phase was concentrated by evaporation and injected into a gas chromatograph. To minimize decomposition of the metal chelates in the injection port and/or the chromatographic column, TFA vapour was introduced into the carrier-gas stream.

EXPERIMENTAL

Instrumentation

The apparatus and operating conditions are shown in Fig. 1 and Table I. A discharge tube was connected directly to the outlet of the column. To prevent the effluent from condensing in the inlet portion of the discharge tube, this was heated at 180° by a small Nichrome-wire heater. To introduce TFA vapour into the carrier gas, argon was passed through the TFA reservoir at a flow-rate of 2 ml/min at 20°. In order to optimize the discharge conditions, more argon was fed to the discharge through a by-pass. The discharge tube was positioned horizontally (perpendicular to the slit), because the spectral emission was not uniform along the length of the discharge. The position of maximum intensity varied with the nature of the metal chelate and with change in the flow-rate of the carrier gas. In this study, for copper and aluminium, the position of maximum intensity was 20-40 mm upstream from the centre of the cavity.

Reagents

Standard solutions of copper and aluminium trifluoroacetylacetonates were prepared by dissolving the pure chelates³ in chloroform; the isotopes copper-64,

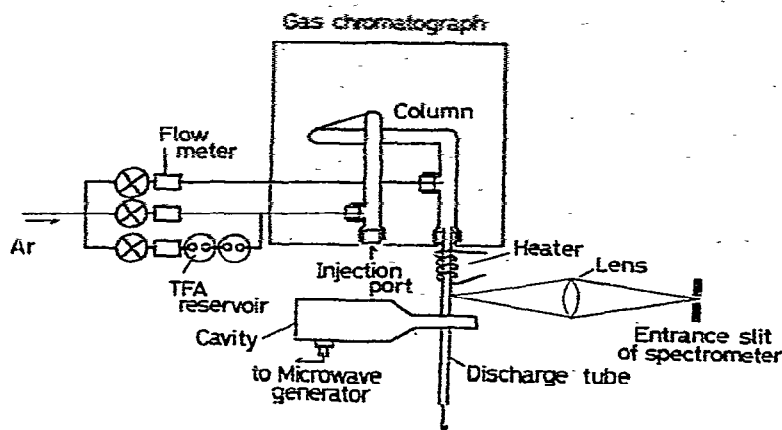


Fig. 1. Schematic diagram of apparatus.

TABLE I
APPARATUS AND OPERATING CONDITIONS

<i>Instrumental component</i>	<i>Description</i>
<i>Gas chromatograph (Yanagimoto GCG 550T)</i>	
Column	45 cm × 3 mm glass tubing; 0.5% of SE-30 on glass beads (60–80 mesh)
Column temperature	140°
Injection-port temperature	180°
Argon flow-rate	Column: 80 ml/min containing TFA vapour (0.05 vol %); by-pass: 40 ml/min
<i>Spectrometer (Nippon Jarrell-Ash JE-50E, 0.5-m Ebert mounting, 1180 lines/mm)</i>	
Slit-width	20 μm
Photomultiplier	Hamamatsu TV R-106
Optics	Quartz lens ($f = 80$ mm; magnification = 1)
Amplifier	NF lock-in amplifier (L I-572A)
Recorder	Toa Dempa EPR-2TB
<i>Microwave generator (Ito Chotampa MR III S; 2450 MHz, 50W)</i>	
Discharge tube	Quartz capillary; 1.6 mm I.D., 4.2 mm O.D., 25 cm long
Cavity	Tapered rectangular (NBS, type No. 1)

iron-59 and zinc-65 were used as tracers. Water was purified by distillation and ion exchange. All other reagents were of analytical grade and were used without further purification.

Analytical procedure

Zinc metal (5 g) was dissolved in 20 ml of *aqua regia*, the solution was evaporated to dryness, and the residue was dissolved in 50 ml of 7 M hydrochloric acid. This solution was transferred to a 200-ml separating funnel and shaken with 50 ml of isopropyl ether for 5 min. A 10-ml aliquot was taken from the aqueous phase, its pH was adjusted to 4.5 with 1.0 ml of 1 M sodium acetate followed by 1 or 6 M sodium hydroxide, then it was transferred to a 30-ml separating funnel and shaken

with 10 ml of 0.1 M TFA-chloroform for 10 min. The organic phase was transferred to a 15-ml glass vial and evaporated to dryness under reduced pressure (≈ 20 mmHg) at room temperature, the residue was dissolved in 0.1 ml of chloroform, and a 1- μ l aliquot was injected into the gas chromatograph. Copper and aluminium were detected by monitoring the emission intensity of the lines at 324.8 and 396.2 nm, respectively.

Calibration graphs (peak height \times half width *versus* quantity of metal) were constructed by injecting 1 μ l of standard solutions of various concentration directly into the gas chromatograph.

To remove small amounts of metals deposited in the injection port and/or the chromatographic column, passage of the carrier gas was continued for 5 min after each experiment.

RESULTS AND DISCUSSION

Chromatograms

Typical chromatograms are shown in Fig. 2.

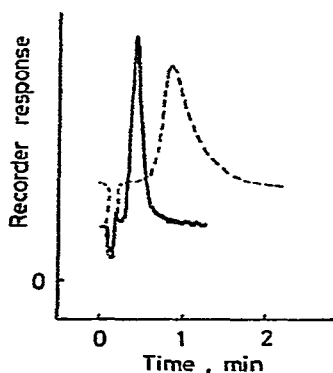


Fig. 2. Chromatograms of a mixture of the chelates of aluminium (full line; 40 ng; 396.2 nm) and copper (broken line; 60 ng; 324.8 nm).

Calibration graphs

Calibration graphs were rectilinear for up to 60 ng of copper and 100 ng of aluminium, and passed through the origin. The errors were *ca.* 8% for 20 ng of copper and *ca.* 10% for 10 ng of aluminium; the lower limits of detection were 1 ng of copper and 0.5 ng of aluminium.

Interference

The iron and chromium chelates were eluted simultaneously with the copper chelate (retention time 0.8 min in our conditions). However, 50 ng of iron and 200 ng of chromium (or 1 μ g of zinc) did not interfere with the determination of 40 ng of copper. Larger amounts of iron enhanced the emission intensity of copper. In the determination of 40 ng of aluminium, the presence of 500 ng of iron and 1 μ g of zinc did not interfere.

Removal of iron

About 80% of the iron present was removed by the single extraction with 50 ml of isopropyl ether from 50 ml of 7 M hydrochloric acid, the loss of copper and aluminium being less than 2%. Repeated extraction was required if the iron content of the zinc metal exceeded 15 ppm.

Extraction of copper and aluminium chelates

Microgram quantities of copper and aluminium were extracted to an extent greater than 95% with 10 ml of 0.1 M TFA-chloroform from 11 ml of aqueous solution in the presence and absence of 1 g of zinc over the pH range 4.5–5.0, less than 1% of the zinc being transferred to the organic phase at pH 4.5. The results agreed with those reported by Scribner *et al.*⁵

The recoveries of copper and aluminium through the whole procedure, excluding the gas chromatography, were greater than 95%.

TABLE II

DETERMINATION OF COPPER AND ALUMINIUM IN A 1-g SAMPLE OF ZINC

<i>Metal added,</i> <i>μg</i>	<i>Metal found,</i> <i>μg</i>	<i>Metal in sample,</i> <i>ppm</i>
<i>Copper</i>		
0.0	2.3	2.3
	2.5	2.5
2.0	4.4	2.4
	4.7	2.7
5.0	7.4	2.4
	7.7	2.7
	Average: 2.5	
<i>Aluminium</i>		
0.0	0.6	0.6
	0.8	0.8
1.0	1.4	0.4
	1.8	0.8
2.0	2.4	0.4
	2.6	0.6
	Average: 0.6	

TABLE III

DETERMINATION OF COPPER AND ALUMINIUM IN COMMERCIAL ZINC GRANULES

<i>Zinc metal</i>	<i>Trace elements</i> <i>found, ppm</i>	<i>No. of</i> <i>determinations*</i>	<i>Relative standard</i> <i>deviation, %</i>
Reagent grade	Cu < 0.1	8	—
(Hayashi Pure Chemical)	Al 8.0		9
Arsenic-free	Cu 2.8	8	11
(Hayashi Pure Chemical)	Al 5.2		11
99.999%	Cu < 0.1	1	—
(Hayashi Pure Chemical)	Al 1.0		—
Reagent-grade	Cu < 0.1	1	—
(E. Merck)	Al 7.9		—

* Duplicate gas chromatographic measurements were carried out for each determination.

Analysis of zinc metal

A sample of commercial zinc metal (Mitsui Mining and Smelting Co., Tokyo, Japan) was analyzed for copper and aluminium by the proposed method; the results are summarized in Table II. Known amounts of copper and aluminium were added before dissolution of the sample. Blank values for both elements throughout the whole procedure were below the detection limits. The average value of 2.5 ppm for copper was in good agreement with the 2.4 ppm value obtained by photometric analysis⁶. The results for several other samples (see Table III) show that the relative standard deviations are about 10% at the low ppm levels. The time required for an analysis is 1–1.5 h.

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