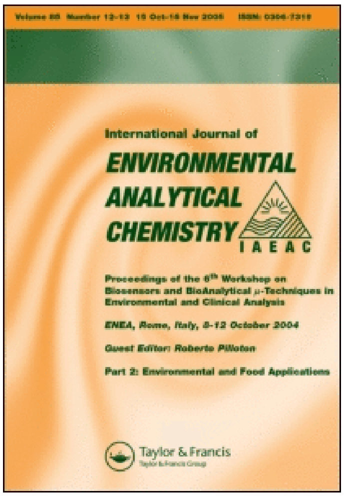

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Determination of Trace Amounts of Antimony by Flameless Atomic Absorption Spectroscopy

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A method for the determination of traces of antimony in organic and inorganic material is described. One gram of the sample is decomposed with sulphuric acid and hydrogen peroxide in a closed system; hydrochloric acid is added and antimony is extracted from the solution with diisopropyl ether. Aliquots of the extract are atomized in a heated graphite tube for atomic absorption measurement. Three possibilities of antimony measurement with detection limits of 0.6, 0.06, and 0.02 mcg per 1 g sample (1 % absorption) are described. The method is suitable for routine work and compares favourably to flame and spectrophotometric methods.

INTRODUCTION

The availability of good analytical methods for the trace analysis of antimony is of prime importance, due to its high toxicity even at trace concentration levels (ppb). The determination of low levels of antimony in food dyes, printing inks and laboratory chemicals is a problem that has not yet been solved satisfactorily. The classical methods, by extraction, complex formation and spectrophotometric evaluation,[1–6] are subject to many interferences. In addition, these methods are not applicable to concentrations below 1 mcg.

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Flame atomic absorption spectroscopy gives improved selectivity, but the sensitivity is not sufficient to estimate antimony at the 1-ppm level from 1 g sample.[7,8] Solvent extraction, followed by direct aspiration of the extract into the flame,[9-12] does not increase sensitivity sufficiently. Detection limits can be improved by the use of an air hydrogen flame.[13] Atomic fluorescence spectroscopy yields better results for a direct measurement of the sample solutions; 0.5 mcg of antimony was given as the minimum detectable amount.[14,15] With the introduction of flameless methods impressive improvements in sensitivity have been reported for antimony,[16,17] with detection limits as low as 5.10^{-12} g. Flameless techniques have been adopted with good success in our laboratories for the analysis of printing inks and TiO_2-containing samples. Some of the problems and results encountered in developing a technique for antimony are described in this paper.

EXPERIMENTAL

Instrumentation

Decomposition of the material was carried out in a closed reflux system described by Gorsuch.[18]

A Perkin-Elmer Model 403 atomic absorption spectrophotometer equipped with a deuterium background compensator and a graphite furnace HGA 70 together with a Perkin–Elmer hollow cathode lamp and a PE 165 recorder were used. The graphite oven has a magnetic valve to stop the inert gas flow during the measurement. Samples (50 mcl) were injected into the graphite oven by Oxford pipettes (Oxford Laboratories, California) with disposable polypropylene tips.

The samples were dried for 60 sec at 100°C, heated for 60 sec 800°C and atomized for 20 sec at 2200°C. Argon was used as inert gas to protect the graphite tube from oxidation.

Instrument settings The spectral line at 217.58 nm was used with a slit width of 0.3 mm (2 Å resolution). Twenty-five per cent absorption was recorded full-scale. Deuterium background compensation was used for all measurements.

Spectrophotometric measurements of antimony were carried out with a Pye-Unicam spectrophotometer SP 600.

Reagents

All chemicals were of analytical-grade purity. All solutions were made from doubly distilled water. A stock solution, containing 1000 ppm of antimony, was prepared by dissolving 2.743 g of antimony tartrate hemihydrate

(Merck, Darmstadt, DBR) K SbO $C_4H_4O_6 \cdot 1/2\ H_2O$ in 200 ml 50% (v/v) sulphuric acid, and diluting to one litre in a volumetric flask. Dilution series were prepared with 1% (v/v) sulphuric acid.

Procedure

Decomposition of the material The sample (1 g, organic or TiO_2) was heated in the decomposition apparatus[18] with 10 ml of 50% (v/v) sulphuric

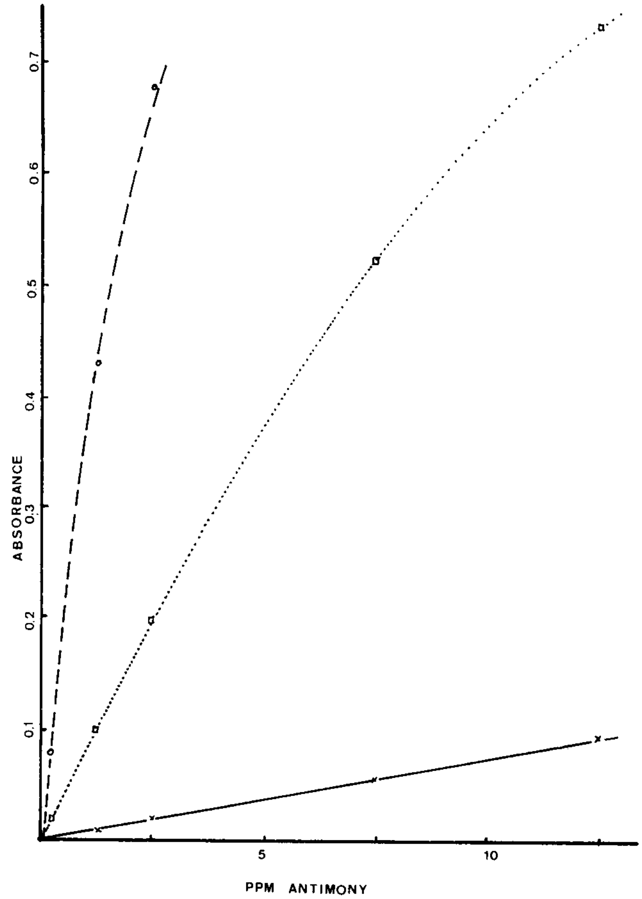

FIGURE 1 Calibration curves for antimony after extraction.

————: Single injection of 50 mcl of the extract into the cuvette.

– – – – –: Four aliquots of 50 mcl of the extract injected into the cuvette, argon flow stopped during atomization.

……………: Single injection of 50 mcl of the extract, argon flow stopped during atomization.

acid. The water was distilled into the reservoir and transferred to a 50-ml measuring flask. The sulphuric acid was then refluxed for a few minutes. After cooling, 0.5 ml of hydrogen peroxide was added and the solution was heated until sulphuric acid fumes appeared. This step was repeated until all organic and inorganic matter had dissolved. The solution was transferred to a 50-ml flask with 32 ml of concentrated hydrochloric acid and diluted to volume with water.

Extraction of antimony The test solution (20 ml) was transferred to a 100-ml separatory funnel, and the following reagents were added: 1 ml 1% (wt) sodium disulphite, aqueous solution; 2 ml 0.2N cerium(IV) sulphate in 1N sulphuric acid; and 2 ml 1% (wt) hydroxylamine hydrochloride, aqueous solution. Then the solution was mixed thoroughly.

Antimony was separated by shaking the solution with 10 ml of peroxide-free diisopropyl ether. The ether layer was washed with 2 ml 10% (wt) sulphuric acid and transferred to a 10-ml polypropylene tube. Reference standards were prepared similarly by extraction from 20-ml portions of 6N hydrochloric acid containing 0, 0.5, 1, and 5 mcg of antimony. Aliquots (50 mcl) of reference and sample extracts were pipetted into the graphite oven and measured. All measurements were made in triplicate.

Evaluation The antimony content of the sample was found from a calibration plot. For low concentrations of antimony, up to four aliquots of 50 mcl of the extract were dried in the graphite cuvette before atomization to improve the detection limit.

The use of a gas stop valve in the argon stream[19] can also improve the sensitivity by a factor of 10 through enhancement of the residence time of the antimony vapour in the cuvette. Typical calibration curves are shown in Figure 1.

Spectrophotometric determination of antimony The determination was carried out by complex formation with rhodamine B after extraction of antimony with diisopropyl ether.[6]

RESULTS AND DISCUSSION

Interferences

During preliminary work in this laboratory, antimony was determined in aqueous solutions which contained high concentrations of hydrochloric, nitric, and sulphuric acid and alkali, iron, and titanium salts; this resulted in serious interferences. With the present procedure, however, interferences from high concentrations of hydrochloric, nitric, and sulphuric acids and salts in the test solution were eliminated. Figure 2 shows the effect of acid concentration on the antimony signal. Water and very dilute acids (less than 0.1%) gave low results due to hydrolysis. Therefore the lowest acid concentration employed was 0.1%.

The presence of hydrochloric acid resulted in low measurements, possibly due to formation of volatile antimony halides; nitric acid caused high values at low concentrations, but showed a strong variation of the values with varying acid amounts. Sulphuric acid gave optimal results. Only small differences in antimony recovery were observed with concentrations of sulphuric acid between 0.1 and 10% (wt). Of the interfering cations, iron and titanium were tested in high concentrations. In Figure 3 it can be seen that in hydrochloric acid solution, interferences are very strong. Addition of 1% (v/v) sulphuric acid to the test solution removes the interference only partially. A direct estimation of antimony in titanium compounds was therefore not possible.

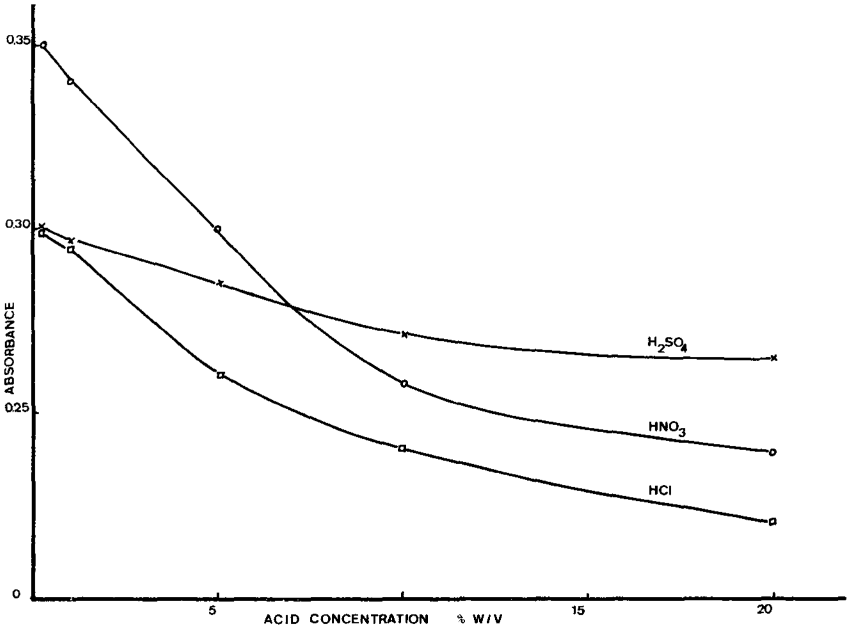

FIGURE 2 Effect of acid concentration on antimony signal. 20 ng of antimony measured. Aqueous solutions were used.

Methylisobutyl ketone, benzene, and diisopropyl ether have been tested for extraction of antimony from hydrochloric acid solutions. Diisopropyl ether gave the best results. Extraction was carried out from 6N hydrochloric acid medium and antimony was determined by atomizing 50-mcl aliquots of the extract. In this procedure, the major problem was the volatility of antimony in the presence of hydrochloric acid during the evaporation step in the graphite tube. This could be eliminated by washing the extract with a small amount of sulphuric acid prior to atomization. Back extraction of antimony by sulphuric acid washing is very small and does not influence antimony values.

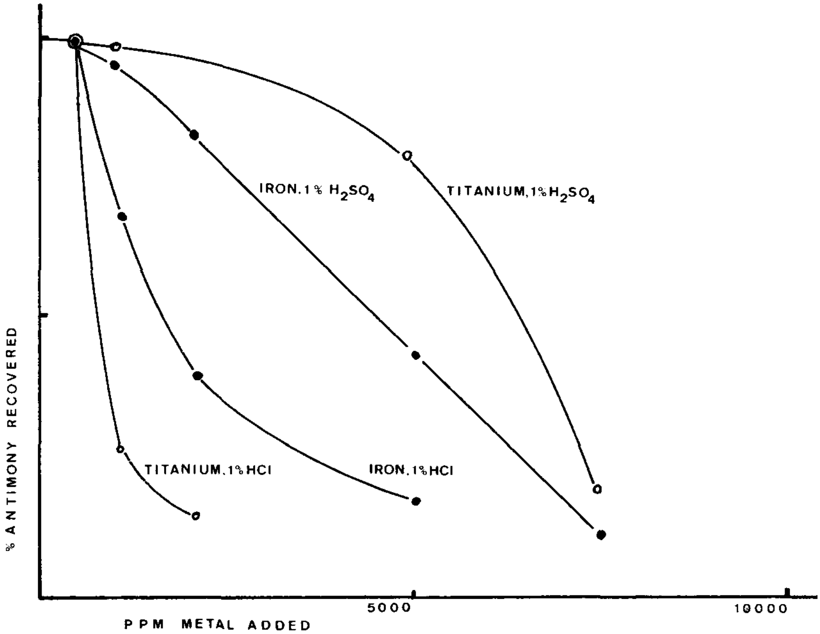

FIGURE 3 Effect of iron and titanium on antimony signal. Recovery of 20 ng of antimony is shown. Aqueous solutions were used.

Analytical Data

The results (Table I) are in good agreement with the values obtained by spectrophotometric analysis. With small samples containing antimony concentrations below 10 ppm, measurement by the proposed method will give more reproducible results than flame methods or spectrophotometric measurements. For 1 g sample, the detection limit was found at 0.6 ppm (= 12 ng of antimony atomized for a 1% absorption signal) using the standard procedure. With the argon flow stop method, the sensitivity can be improved and a detection limit of 0.06 ppm (1.2 ng antimony atomized) has been observed.

TABLE I

Results of antimony determination with a graphite furnace compared to a spectrophotometric assay[a]

Sample material	Sample size	ppm Sb HGA 70	ppm Sb spectrophotometric
TiO_2 I	1 g	9.5 ±0.5	9.4±1.3
TiO_2 II	1 g	12.2 ±0.6	10.6±1.2
TiO_2 III	0.2 g	42±2	45±3
$TiCl_3$, 15% solution	5 ml	1.6 ±0.1	2.3±0.5
Printing ink (20% TiO_2)	1 g	3.5 ±0.2	3.8±0.6
Hydrochloric acid (reagent grade)	20 ml	0.03±0.01	not detected

[a] Mean values and S.D. of eight determinations are listed. Single injection procedure was used.

Injection of four aliquots of 50 mcl into the graphite tube in combination with argon flow stop yielded a detection limit of 0.02 ppm. With these three possibilities of measurement, the method can easily be fitted to a wide range of antimony concentrations without altering the procedure.

Due to the preparation of the sample in a closed system, no antimony losses occurred even with materials with high halogen concentration or high amounts of organic material. Interferences by other elements were minimized by the extraction step and the high selectivity of atomic absorption measurement. The method can be considered suitable for routine work.

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