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ATOMIC ABSORPTION DETERMINATION OF MICROALLOYING ELEMENTS IN STEELS BY DISCRETE SAMPLE NEBULIZATION

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ABSTRACT

A rapid atomic absorption procedure for the determination of microcomponent elements (aluminum, antimony, arsenic, cobalt, lead, tin, and vanadium) in steels by discrete sample nebulization is described. Direct injection of microsamples was employed for metallic elements. Detection limits were in the range 0.005%–0.0005%. Iron matrix interferences were compensated for by means of background correction and the method of standard additions. A branched capillary, which permitted the simultaneous nebulization of a carrier stream of sodium borohydride solution and a microsample volume, was tested to enhance the sensitivity in the determination of arsenic.

INTRODUCTION

Low-alloy steels are employed in nuclear industry for the construction of pressure vessels for nuclear power reactors. Some elements, usually present at low concentration levels, have a marked influence on the mechanical properties and radiation damage characteristics of those materials. Consequently, methods are required for rapid chemical characterization of steels related to nuclear technology applications.

Among the numerous flame atomic absorption techniques applied for steel analysis, discrete sample nebulization (1–4) offers several distinct advantages, permitting the direct injection of highly acidic, high salt-containing solutions required to attain low levels of detection. Clogging of the nebulizer and corrosion risks, arising from the high acid content of the solutions, are reduced. Additionally, in situ microdilutions and microstandard additions (3) can easily be performed to expedite the determinations.

A single pulse nebulization technique for the atomic absorption determination of aluminum, arsenic, and tin in steels was reported by Thompson and Godden (5). Zhou et al. (6) described a method based on pulse nebulization for the determination of trace lead, bismuth, antimony, and silver in steels. Microsamples are injected into a carrier stream of distilled water by means of a flow injection technique.

Low concentrations of arsenic, tin, and aluminum have been determined in steels by Matsubara et al. (7). Hydride generation was employed for the first two elements and an injection method for aluminum.

The present paper deals with the direct determination of (soluble) aluminum, antimony, arsenic, cobalt, lead, tin, and vanadium in steels by flame atomic absorption spectrometry. Metallic elements were determined by a discrete sample nebulization technique. Regarding arsenic, Xian-An et al. (8) have observed an increase in sensitivity in the atomic absorption determination of some hydride-forming elements when their solutions are nebulized simultaneously with a potassium borohydride solution. A twin-spray apparatus, consisting of a Y-piece bifurcate capillary, was employed by those authors. Consequently we tested a branched capillary (9) to enhance sensitivity in the determination of arsenic. By means of a simple device, a sample microvolume is injected by pneumatic suction into a carrier stream of sodium borohydride solution and nebulized into a nitrous oxide-acetylene flame.

EXPERIMENTAL

Apparatus

A Model 82-500 Jarrell-Ash atomic absorption and emission spectrometer, equipped with single element hollow cathode lamps, was employed. The spectrometer was operated at maximum sensitivity with an air-acetylene or a nitrous oxide-acetylene flame (premix burner). Peak absorbances were measured using a strip-chart recorder. Analytical wavelengths and flame type are listed in Table I. Nonspecific background absorption at or near the analyte wavelength was measured by means of the continuum emitted by a hydrogen discharge lamp (in hollow cathode configuration) or nonabsorbing lines from the single element hollow cathode lamps.

A Teflon microsampling cone (3) (2 cm height, 2 cm diameter, 1 cm deep) was employed to nebulize up to 250-µL solutions, dispensed with Eppendorf micropipettes. Sampling manifolds, as described by Eaton and Schiemer (10) or Matusiewicz (11), can also be conveniently applied to the same purpose.

For arsenic determination, a T-piece connector (Figure 1) made of Teflon was directly fitted to the nebulizer capillary tip. Lateral branches consisting of two #10 syringe needles were attached to plastic capillary tubing. The device was employed to simultaneously deliver a carrier stream of sodium borohydride solution through one of the branches and a microsample from a microcone through the other. The position of the carrier solution reservoir relative to the sample manifold was conveniently adjusted to avoid siphoning. (12).

Reagents

All reagents and chemicals were of analytical reagent grade. Water was demineralized and redistilled in quartz.

Stock analyte solutions (1 mg/mL) were prepared from Merck Titrisol, with the exception of arsenic for which a 914-µg/mL solution (Alfa Products) was employed. Sodium borohydride (Alfa Products) solutions were freshly prepared, stabilized by adding a potassium hydroxide pellet for each 100-mL 1% (w/v) solution (13), and filtered through a 0.45-µm Millipore filter.

For background absorption interference studies, high purity iron was used to obtain matrix solutions of different concentrations.

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TABLE I
Analytical Wavelengths and Procedures for Background Correction

Element	*Flame type*[a]	*Analytical line (nm)*	*Wavelength for background correction (nm)*
Al	N-A	309.3	Not required
As	N-A	193.7	H continuum 193.7
Co	A-A	240.7	H continuum 240.7
Sb	A-A	231.2	H continuum 231.2
Sn	N-A	235.5	H continuum 235.5 (or Sn 235.5[b])
Pb	A-A	217.0	H continuum 217.0
V	N-A	318.4	Not required

[a] N-A: nitrous oxide-acetylene; A-A: air-acetylene.
[b] Background measured with a high purity Fe solution of same concentration as the sample.

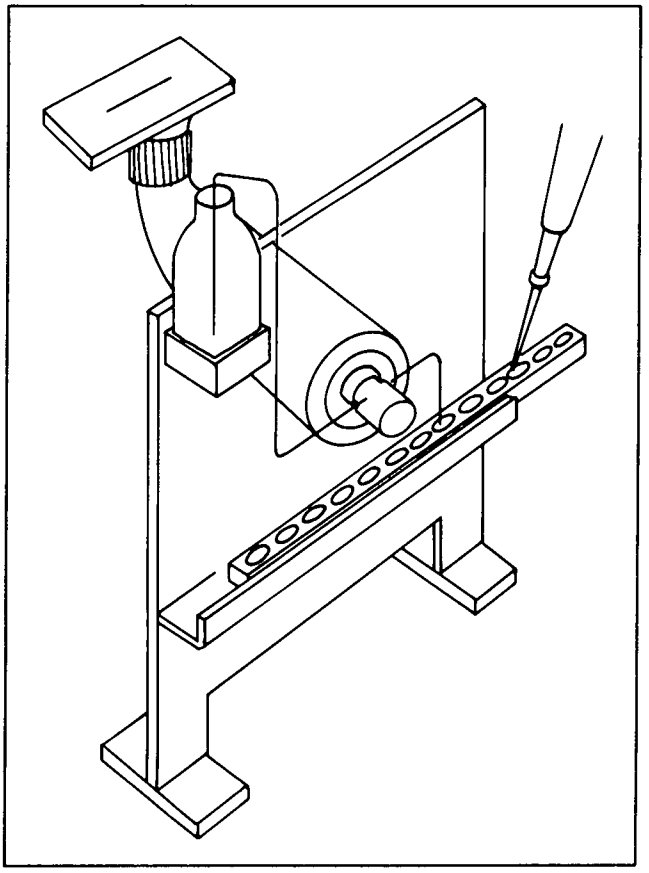

Fig. 1. T-piece capillary and sample manifold used for arsenic determinations.

PROCEDURES

Steel samples (usually 5.0 g, weighed to 1 mg) were dissolved in aqua regia as recommended in (5), and finally diluted to 50 mL with water. When necessary, a Teflon-lined pressure bomb (Spex Industries) was used for dissolution of smaller samples (about 1.0 g) to avoid losses of arsenic. In this case, the final volume was 10 mL. These solutions were diluted according to the concentration of the determined elements. Blank solutions were prepared with similar amounts of the acids. Sample and blank solutions were stored in plastic bottles.

Optimization of operating conditions, in particular the volume and flow rate of the nebulized solutions and the response time of the spectrometer recording system, was carried out as previously described (14).

The continuum emission from the hydrogen-filled hollow cathode lamp, operated at 24 mA, was used to investigate the background absorption contribution at different wavelengths. With a 0.8-nm monochromator spectral bandpass, absorbance measurements were performed between 190 and 340 nm for nebulization of 100-μL volumes of a 10% (w/v) iron solution containing hydrochloric and nitric acids.

Analytical calibration for individual elements was carried out by a microstandard addition procedure (14). Curves were constructed usually with three calibration points, each one the average of three or four replicate peak absorbance measurements. Individual absorbances were background corrected when required by subtracting a mean nonspecific absorbance estimated at the appropriate wavelength (Table I). This value was obtained by averaging the data from replicate injections of a sample solution with no added analyte.

Sample concentration values were calculated by extrapolation of calibration straight lines fitted by a least-squares procedure. The method used by Larsen et al. (15) was employed to estimate confidence limits.

RESULTS AND DISCUSSION

Selection of Sample Volume for Determination of Metallic Elements

Curves of absorbance vs. injected volume were obtained by nebulization of a 2-μg/mL copper solution for variable aspiration rate and response time of the signal recording system, as described in a previous work (14). For routine operation, a minimum damping setting, a solution aspiration rate of 3.7 mL/min, and injection volumes of 100–200 μL were selected.

Background Interferences

Nonspecific absorption is the most severe limitation in discrete sample nebulization because of the high solid content

of the injected solutions. This additive interference is critical when the standard addition method is employed for calibration. When an iron matrix is nebulized in an air-acetylene flame, background absorption is generated by molecular species and weakly absorbing iron lines falling within the monochromator spectral handbass.

The background absorbance, measured with the hydrogen continuum source, vs. wavelength is shown in Figure 2. Data were obtained by injecting 100-µL volumes of a 10% (w/v) iron solution. It can be deduced from the plot that background correction is required for the elements (cobalt, antimony, and lead) determined by atomization in the air-acetylene flame. The FeO molecule is considered the origin of the strong band absorption observed at around 240 nm. Similar results have been reported by other authors (16) for continuous nebulization of iron solutions.

Signal-to-noise ratios were evaluated for background peak absorbances measured at the analytical wavelengths using the hydrogen lamp; or at nearby wavelengths using nonabsorbing element lines emitted by the analyte hollow cathode lamps. For most elements, agreement within 5% relative absorbance was observed for both measurement procedures. Background wavelengths giving the best results are listed in Table I. Nonspecific absorption was found to depend critically upon the spectral bandpass in the case of cobalt. A 0.08-nm value of that parameter was selected for both line and background measurements.

Owing to the higher vaporization-atomization efficiency of the nitrous oxide-acetylene flame and the shorter optical path (5 cm slot burner), background contribution from this flame was under the noise level, except for tin. Because iron with a negligible content of tin was available, correction could also be performed by subtracting the absorbance at the analytical wavelength produced by an iron solution of the same concentration as the sample solution.

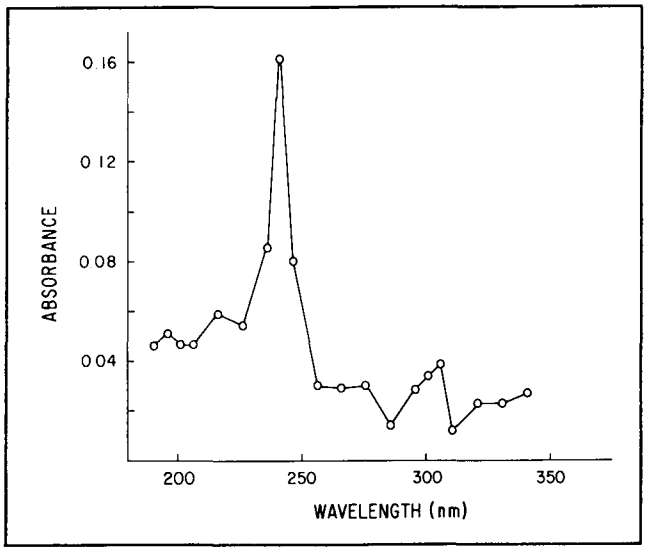

Fig. 2. Dependence of background absorbance upon wavelength for a 10% (w/v) iron solution.
Flame: air-acetylene. Volume nebulized: 100 µL.

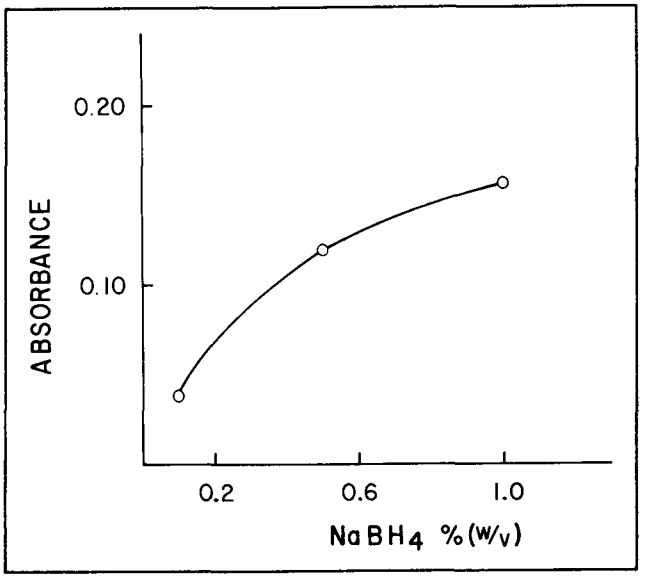

Fig. 3. Variation of arsenic absorbance vs. concentration of sodium borohydride in the carrier stream. Sample: 17-µg/mL As solution in 20% (v/v) solution. Volume nebulized: 100 µL.

Determination of Arsenic

The simultaneous aspiration of a sodium borohydride solution and a microvolume of sample containing arsenic enhances the absorbance signal for this element. Atomization is favored through the generation of volatile hydride at the tip of the nebulizer. A similar effect has been reported (8) for antimony and bismuth solutions continuously nebulized in an air-acetylene flame.

We tested the bifurcate capillary used in the present work by injecting volumes of between 5 and 200 µL of a 66-µg/mL arsenic solution. The concentration of the sodium borohydride carrier stream was varied between ~0.2 – 1.0%. Peak absorbances were recorded for different damping settings and aspiration rates.

For arsenic solutions prepared in hydrochloric acid, peak absorbances were almost independent of the acid concentration between 10 and 20% (v/v). Maximum signal-to-noise ratio was obtained for an aspiration rate of 5 mL/min and for a damping setting corresponding to a full-scale response time of 4 s on the recorder. A curve of absorbance vs. nebulized volume leveled off at about 100 µL and this sample injection volume was selected for routine operation.

Absorbance varied with the concentration of sodium borohydride in the carrier stream (Figure 3). A concentration of 1% (w/v) was the highest value tested, compatible with normal operation of the nebulizer and acceptable flame flicker noise.

Analytical calibration curves were constructed for arsenic solutions containing 10% (v/v) hydrochloric acid in the absence and presence of 10% (w/v) iron, using water or 1% (w/v) sodium borohydride as a carrier stream. Linearity was observed for arsenic concentrations in the range 0–20 µg/mL. When water was used as carrier and an iron-free arsenic solution was injected, the characteristic concentration was 3.5 µg/mL. This value improved to 0.5 µg/mL for 1% (w/v) sodium borohydride, but was degraded to 1.5 µg/mL when the injected arsenic solutions contained 10% (w/v) iron. Curvature in the calibration graph was observed for the combination of sodium borohydride carrier-arsenic solution (free of iron) above 20 µg/mL (0.2 absorbance) of arsenic due to

the sluggish response of the signal recording system. However, this fact would not preclude employing the calibration curve procedure for analysis of pure arsenic solutions.

Background absorbance was below the noise limit for iron concentrations up to 4% (w/v). For higher iron concentrations, correction can be performed by using the hydrogen lamp. The average background absorbance value for a solution of 10% (w/v) iron was 0.018. Precision of peak absorbance measurements for arsenic in 10% (w/v) iron is limited by the relatively poor stability of the hollow cathode lamp emission at 193.7 nm and the low response of the photomultiplier tube (1P28) at that wavelength. In addition, small bubbles generated by the decomposition of the sodium borohydride solution and carried by the solution stream cause an increase in the flame flicker noise. All of these factors resulted in a maximum relative standard deviation of about 10% [measured with 6 replicate injections of a 42-μg/mL solution of arsenic, 9% (w/v) iron, and 10% (w/v) hydrochloric acid].

To check whether precision could be improved through peak area measurements, absorbances for the same solution and operating conditions were recorded using a high recorder chart speed: areas under the peaks were evaluated by means of an electronic digital planimeter (Kontron). A relative standard deviation of 5.8% was obtained. It can be concluded that considerable improvement in precision should be expected for modern instrumentation counting on a more stable excitation source (i.e., EDL) and signal integration (17).

Detection Limits

Detection limits were estimated for each element based on three times the standard deviation of the background signal in an iron-containing blank. The maximum iron concentrations tested are shown in column 2 of Table II. These concentrations were at least as high as those encountered in real production samples. No attempts were made to use higher iron concentrations in the case of the Al determination. Background correction problems are expected for Co and Sb with solutions containing iron concentrations higher than 5% (w/v), because the analytical lines of these elements are located within the strong background absorption region (see Figure 2).

TABLE II
Detection Limits[a]

Element	Iron concn in blank soln (% w/v)	Detection limit (ng)	Detection limit (%)
Al	5	150	0.003
As	9	450	0.005
Co	5	45	0.0009
Sb	5	300	0.006
Sn	9	260	0.003
Pb	9	45	0.0005
V	9	400	0.004

[a] Volume nebulized: 100 μL.

Application to Steel Samples

Comparative results, performed on a steel production sample, between atomic absorption concentration values and those obtained by a spark atomic emission spectrometric technique are given in Table III. Comparison was limited to those elements for which suitable solid reference samples were available for the atomic emission procedure.

Recovery tests were performed by the atomic absorption procedure for antimony on spiked sample solutions containing residual amounts of this element due to the unavailability of reference samples in the low concentration range. For added amounts of antimony, equivalent to element concentrations ranging from 0.023 to 0.046% on sample basis, recoveries varied from 91 to 104%.

Determinations were carried out for the remaining elements on BCS and NBS standard reference materials (Table IV). Calibration was performed by the standard addition procedure. Precision for individual determinations was estimated by calculation of confidence limits for the 95% probability level according to the method of Larsen et al. (15). Agreement between reported and found values is acceptable, confirming the aptitude of the procedure for the rapid chemical characterization of steels required in some corrosion and fragility studies.

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TABLE III
Comparison With Spark
Atomic Emission Spectrometry

Element	Concentration measured (%): Atomic emission	Concentration measured (%): Atomic absorption
Al	0.013	0.014 ± 0.003
Co	<0.01	0.0054 ± 0.0011
Sb	<0.05	<0.02[a]
Sn	<0.003	<0.009[a]
V	0.02	0.016 ± 0.003

[a] Less than limit of quantitation.

TABLE IV
Analysis of Standard Reference Materials

Element	Reference sample	Concentration (%): Reported	Concentration (%): Found
Al	NBS-461	0.005	<0.01[a]
As	NBS-461	0.028	0.030 ± 0.011
Co	BSC-337	(0.034)[b]	0.031 ± 0.005
	NBS-461	0.26	0.23 ± 0.04
Pb	NBS-461	(0.003)[b]	0.003 ± 0.002
Sn	BCS-241/2	0.025	0.022 ± 0.004
	NBS-461	0.022	0.019 ± 0.003
V	BCS-337	(0.02)[b]	0.017 ± 0.005
	NBS-461	0.024	0.024 ± 0.006

[a] Less than limit of quantitation.
[b] No certified value.

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