The determination of antimony in lead??? antimony alloys using ICP-OES and internal standardisation

2 AUTHORS:

Marius Harmse

1 PUBLICATION   10 CITATIONS

SEE PROFILE

Robert I Mccrindle

Tshwane University of Technology

101 PUBLICATIONS   764 CITATIONS

SEE PROFILE

The determination of antimony in lead–antimony alloys using ICP-OES and internal standardisation

Marius J. Harmse and Robert I. McCrindle*

Department of Chemistry and Physics, Technikon Pretoria, Private Bag X680, Pretoria 0001, South Africa. E-mail: mccrindle@techpta.ac.za

Lead–antimony alloys are used in certain applications where ductile alloys are required. The physical properties of the alloy will depend primarily on the chemical composition, in this case, the amount of antimony present. Antimony will inhibit corrosion, change the density, and also increase the hardness of the alloy. An analytical test procedure making use of an inductively coupled plasma optical emission spectrometer (ICP-OES) was needed for the accurate and precise determination of the antimony content of lead–antimony alloys. The sample for analysis was prepared with an internal standard and quantified using an ICP-OES. Cadmium was selected as internal standard because it emits at a wavelength close to antimony and it has a first ionisation potential almost the same as antimony. Three certified reference materials were analysed. The results obtained for three reference materials were precise and accurate. Day-to-day repeatability was better than 1.4% m/m. Within-day repeatability of an alloy was 0.016% m/m.

Introduction

Lead–antimony alloys are used for the manufacture of batteries and ammunition. The antimony content determines their physical properties. There is considerably more literature regarding these properties[1,2] than analytical methods to determine the concentration of the antimony.[1] The performance of the alloy relies upon its physical properties, hence, a robust, accurate and precise method for the quantification of the antimony was required. The antimony concentration usually lies between 1 and 10% m/m with a specification of $\pm 0.2\%$ m/m and an allowable deviation of 0.3% m/m (acceptable test results lie within $\pm 0.3\%$ m/m). The repeatability of the method should consequently be 0.2% m/m or better.

Analytical methods using ICP-OES and direct calibration procedures did not give sufficiently precise and accurate results (RSD > 1%). The aim of this investigation was to develop a method for the preparation and dissolution of the sample, as well as quantification of the antimony content, within the level of repeatability required, but still making use of an ICP-OES as the company did not wish to consider other techniques, such as X-ray fluorescence (XRF). An internal standard material was investigated because this usually increases the integrity of results. The instrumental procedure was then optimised.

Certain points should be considered before using an internal standard in ICP-OES analyses. The internal standard element should have essentially the same behaviour as the analyte in the plasma, as well as in the nebuliser. Concentrations should also be similar to prevent problems with nebulisation. If there is a large concentration difference, enrichment or depletion of the analyte may occur in smaller droplets in the aerosol.[3–6]

Ions and atoms may behave differently in the plasma and the analyte and internal standard lines should consequently have first ionisation potential almost the same, irrespective of whether ion or atom lines are used.

A mathematical model for internal standardisation was developed. Since all measurements were done by mass determinations, these quantities were related to the spectral line intensities obtained to devise a calibration curve.

The test procedure using lead-antimony alloy was verified using certified reference materials.

Experimental

Instrumentation

An ARL 3580 ICP-OES with one monochromator, one polychromator, and retrofitted electronic circuitry was used. It was possible to integrate one channel on the monochromator while integrating the channels on the polychromator, as long as the integration times were the same. The monochromator was used for optimisation, the polychromator for final analysis.

Nebuliser

The peristaltic pump used to feed the sample to the nebuliser was a Gilson Miniplus 4 (from Lasec, South Africa) with peristaltic tubing of 0.89 mm inner diameter (orange–orange). The pump was calibrated to relate revolutions min^{-1} to a flow rate in $l\,min^{-1}$, using a stop watch and weighing the amount of water consumed in a certain time.

The optimisation of the nebuliser was done by first establishing the noise associated with a certain sample flow rate. A solution containing Cd (about 50 mg dm^{-3}) was aspirated at different flow rates. Ten consecutive integrations (on peak) of one second each were made at different sample flow rates and the %RSD of the peak intensities were calculated and plotted against the sample flow rate. The flow rate where the %RSD of the integration readings was the least was determined.

The next step was to determine the spectral line intensity at a certain sample flow rate. This was done by aspirating the same Cd solution and integrating (on peak) the Cd I 228.802 nm spectral line at different sample flow rates. The peak intensities were plotted against the corresponding sample flow rate. The graph obtained was used to decide the optimum flow rate, *i.e.*, where the highest signal is obtained without aspirating too much sample.

The results of both of the above procedures were used to decide the optimum flow rate.

Spectral line selection

It is suggested that an analytical spectral line and an internal standard spectral line with corresponding properties should be

used. The two lines chosen were Sb I at 206.833 nm (excitation potential, E_{ep} 5.994 eV, and first ionisation potential, E_{ip}, 8.641 eV) and Cd I at 228.802 nm (E_{ep} 5.419 eV, E_{ip}, 8.641 eV).[7] Cadmium could be considered as internal standard as none of the samples contained the element.

The spectral emission lines were found to be free from interferences that may have occurred as a result of other species or elements in solution.

Solutions

Water used throughout the study was deionised (<18 MΩ cm) and A-grade glassware (Glassworld, South Africa) was used. The internal standard stock solution was prepared by dissolving 1.0 g of cadmium metal (Sigma-Adrich, Atlasville, Kempton Park) in 50 ml 1 : 1 HNO_3 (Analytical Grade, Merck, S. A.) in a beaker on a hot plate. After dissolution, the cooled cadmium solution was transferred to a 200 ml volumetric flask filled to the mark with water.

A calibration standard stock solution was prepared by measuring 1.1 g of antimony metal (Sigma–Aldrich) accurately into a 100 ml volumetric flask. To the antimony in the volumetric flask about 2.5 g of tartaric acid and 25 ml HNO_3(c) was added. A further 5 ml of HCl(c) (Analytical Grade, Merck, S. A.) was added slowly. After the addition of the HCl, the volumetric flask was placed into a large beaker containing warm (not hot) water and the dissolution was continued. The temperature was kept below about 80 °C, because antimony forms volatile chlorides at about 140 °C.

Calibration standard solutions were prepared by weighing the calibration standard stock solution into clean, marked, 200 ml volumetric flasks. Seven calibration standard solutions were prepared by weighing (to the nearest 0.1 mg) 0, 1, 2, 3, 4, 5 and 6 g of the calibration standard stock solution into each volumetric flask, respectively. Thereafter, 2 g of the Cd internal standard solution was weighed (to the nearest 0.1 mg) into each flask. The volumetric flasks were each filled to the mark with water. The concentration of the antimony was calculated and expressed as mg Sb ml^{-1}.

The acid for dissolution was prepared by mixing 1000 ml of $HNO_{3(c)}$, 1000 ml water, and 80 g tartaric acid.[8]

Sample preparation

Each sample of alloy was in the form of a button, about 45 mm in diameter and 18 mm high. Small, thin pieces were drilled from the button for analysis. These pieces were collected and accurately measured (to the nearest 0.1 mg) into a 100 ml flask. The Cd internal standard solution (1 g) was accurately weighed (to the nearest 0.1 mg) into the flask. Five millilitres of dissolution acid were added and the flask placed on a hot plate (at low temperature) to dissolve. About 100 ml of water was added to the flask and swirled to mix thoroughly.

The mass of sample taken depended upon the expected antimony concentration. For antimony concentrations in the range of about 2% m/m, about 1 g was taken; for 3.5% m/m, about 0.57 g and for 10% m/m, about 0.2 g was used.

Certified reference materials (CRMs) (MBH Analytical England) were prepared in exactly the same fashion.

Instrumental parameters

Simultaneous measurements were performed on both Cd and Sb spectral lines (on peak), according to the parameters shown in Table 1.

Calibration

Calibration was performed by running the calibration standard solutions and measuring both the Cd and Sb spectral line intensities and calculating the ratio according to the following

Table 1 Plasma instrumental parameters

Parameter	Value
Rf power	1250 W
Aerosol carrier gas flow rate	0.4 l min^{-1}
Auxiliary gas flow rate	0.8 l min^{-1}
Argon plasma gas flow rate	15 l min^{-1}
Nebuliser	Meinhard
Spray chamber	Mini, single pass, with impact bead
Torch	16 mm id

equation

$$IR = 100 \ ab/cd$$

where IR is the intensity ratio, a the Sb peak intensity (kcps), b the Cd internal standard solution mass (g), c the volume diluted (ml) and d the Cd peak intensity (kcps).

The intensity ratio obtained for each calibration standard solution was plotted against the calculated concentration. Linear regression analysis was performed to calculate the numerical calibration curve, the regression coefficient, limit of detection, and various other numerical parameters.

The samples and CRMs were aspirated into the ICP-OES and the measurements were repeated. The numerical calibration parameters were used to calculate the final antimony concentration in each sample and CRM.

Unknown samples and certified reference materials

To verify the validity of the test procedure and results obtained, CRMs were analysed together with in-house samples. Three tests were performed. The first was the within-day repeatability, the second was to ensure the ruggedness of the procedure, day-to-day repeatability. The third test was for accuracy, using CRMs.

To perform the within-day repeatability, a single sample (sample ID: BTC 2% K37 PM2) was prepared 12 times and analysed all within one day. Calibration data were collected by aspirating the calibration standard solutions and thereafter the unknown samples were aspirated. The Sb concentration of each unknown sample was calculated using this data. The day-to-day repeatability was established by preparing two samples (sample ID: BTC 2% K37 PM2; and sample ID: BTC 9% 724 A BK) on 8 different days. Each day a set of calibration data was collected and the unknown samples were then aspirated as well. The Sb concentration of each was calculated.

One set of CRMs was aspirated each day together with the in-house samples and the respective Sb concentrations calculated as well.

Statistical analysis

The calibration curve is defined as $a = y - bx$, where b is the sensitivity. Regression, r, is such that $r = S_{xy}/\sqrt{S_{xx} \ S_{yy}}$, and S is the error in that value.[9]

$$S_b = S_r/\sqrt{S_{xx}} \text{ and}$$

$$S_a = S_r/\sqrt{\sum x_i/n \ S_{xx}}$$

The limit of detection (LOD) is given by LOD $= 3S_r/b$ and the limit of quantisation (LOQ) is LOQ $= 10S_r/b$.

Results and discussion

Nebuliser

The nebuliser and spray chamber were optimised by first performing 10 consecutive integrations at different sample flow

Table 2 Numerical parameters of the calibration curves over nine days

Day	$a \times 10^3$	$b \times 10^3$	r^2	$S_a \times 10^4$	$S_b \times 10^6$	$S_r \times 10^4$	LOD/mg dm^{-3}	LOQ/mg dm^{-3}
1	6.677	1.755	0.999994	1.310	0.7264	4.297	0.74	2.5
2	6.087	1.730	0.999988	2.209	1.140	6.162	1.1	3.6
3	6.226	1.742	0.999988	1.831	1.015	6.005	1.1	3.5
4	7.193	1.733	0.999986	1.963	1.088	6.435	1.2	3.8
5	7.021	1.729	0.999985	1.769	0.9805	5.800	1.1	3.4
6	6.749	1.729	0.999992	1.499	0.8310	4.916	0.85	2.9
7	7.595	1.806	0.999985	2.196	1.217	7.199	1.2	4.0
8	7.057	1.832	0.999985	2.197	1.218	7.202	1.2	4.0
9	6.803	1.770	0.999984	2.275	1.261	7.459	1.3	4.4

rates and calculating the %RSD of each set of measurements. The data was plotted and from the graph it was found that above about 1000 1 min^{-1} the %RSD did not decrease significantly. A flow rate of 1400 1 min^{-1} was chosen.

To obtain the best spectral line peak intensity, a similar procedure was followed to that described above. The averages of ten consecutive 1 s integrations (on peak) were plotted against the sample flow rate. Increasing the flow rate beyond about 1000 1 min^{-1} did not result in a significant increase in spectral peak intensity. It was decided to still use a sample flow rate of about 1400 :l min^{-1} after considering the data.

Line selection

The spectral lines described above, selected according to spectral line libraries, were free from interferences. There were no spectral interference from the matrix (i.e., Pb), Sb, or the plasma itself (molecular species like OH, N, NH or NO, or atomic Ar) on the Cd I 228.802 nm line. The background was also very low (<1 kcps).

The same procedure was followed to investigate the Sb 206.833 spectral line and again no spectral interferences were found. The background was also low (<1 kcps).

Calibration

Several calibrations were performed. Each day the calibration standard solutions were aspirated and their data collected before the unknown samples and CRMs were aspirated. The numerical parameters are presented in Table 2.

With-in day repeatability

One sample (ID: BTC 2% K37 PM2) was prepared 12 times and the antimony concentration quantified within the same day. Five replicate integrations were made on each sample. The results are summarised in Table 3.

Table 3 Descriptive statistics for within-day repeatability using BTC 2% K37 PM2

Minimum	1.922% m/m	Confidence level	95%
Maximum	1.939% m/m	Number of observations	12
Median	1.931% m/m	t_{calc}	2.201
0	1.928% m/m	Confidence limit—low	1.925% m/m
s	0.0050% m/m	Confidence limit—high	1.931% m/m
%RSD	0.259	Repeatability	0.016% m/m

At the 95% confidence level, results from this specific sample should lie between 1.925 and 1.931% m/m.

Day-to-day repeatability

Two samples (ID: BTC 2% K37 PM2 and BTC 9% 724 A BK) were prepared on 8 different days and the amount of antimony quantified. Calibration standard solutions were run each day before the unknown samples were measured; 5 consecutive integrations were performed and the averages and standard deviations were based on these values. The results of inferential statistical analyses were performed on both sets of data (samples ID: BTC 2% K37 PM2 and BTC 9% 724 A BK) and may be found in Table 4. Consequently, if the samples are repeated the next day, 95% of the time the two results should not differ by more than 0.012 and 0.130% m/m, respectively.

Certified reference materials

Three CRMs were analysed. The results were based on five repeated integrations.

A summary of the data obtained may be found in Table 5.

Inferential statistical analyses were performed on each CRM and an experimental value obtained. Set 1 is the experimental values, set 2 is the certified values. The application of these results to Student's *t*-test can be found in Table 6. Close examination showed that all the CRMs have results that correlate with the certified values (as proven by the *t*-tests). It can, therefore, be deduced that this method produces accurate results.

The results of one CRM (81 X PA 3.5) were constantly much higher than expected. The certified result is 3.5% m/m, while the average value obtained is 3.581% m/m.

All data, although not shown, were tested for outliers. The ATSM method for rejection or retention of outliers was used (so-called T_n-test).

Conclusion

The test method described produced results that were reliable from day to day, as well as accurate and very precise. It is a method that can be used in a routine laboratory to quantify the antimony concentration of lead–antimony alloys, and in so doing predict the physical properties of the alloy. High quality alloys can be produced when this test procedure is incorporated in production quality control.

The calibration curves obtained were highly linear with a

Table 4 Descriptive statistics for day-to-day repeatability using BTC 2% K37 PM2 and BTC 9% 724 A BK

	PM2 (% m/m)	A BK (% m/m)		PM2	A BK
Minimum	1.916	9.387	Confidence level	95%	95%
Maximum	1.927	9.496	Number of observations	8	8
Median	1.922	9.442	t_{calc}	2.365	2.365
0	1.921	9.451	Confidence limit—low	1.918	9.419
s	0.0037	0.0390	Confidence limit—high	1.924	9.484
%RSD	0.191	0.412	Repeatability	0.012	0.130

Table 5 Summary of the results for the analysis of three CRMs, 81XPA 2.0, 81XPA 3.5 and 81XPA 10.0

CRM	Minimum value (% m/m)	Maximum value (% m/m)	Median (% m/m)	0 (% m/m)	%RSD	Certified value (% m/m)
81XPA2.0	2.014	2.023	2.017	2.017	0.142	2.00 ± 0.05
81XPA3.5	3.571	3.586	3.585	3.581	0.170	3.50 ± 0.09
81XPA10.0	10.03	10.09	10.08	10.07	0.199	10.0 ± 0.25

Table 6 Application of Student's *t*-test

CRM	0_1 (% m/m)	0_2 (% m/m)	s_1	s_1	t_{calc}	t_{crit}
81XPA 2.0	2.017	2.0	0.0029	0.05	0.755	2.776
81XPA 3.5	3.581	3.5	0.0061	0.09	2.014	2.776
81XPA 10.0	10.07	10.0	0.0200	0.25	0.971	2.776

correlation coefficient of at least 0.999992, and detection limits of better then 1.3 mg dm^{-3} (in test solutions). Although the detection limits were not of real significance in this test, it gives an indication of the linearity of the calibration curves.

The test method can be adapted to quantify major components of other metal alloys, as long as assiduous attention is given to details such as ionisation and excitation energies of both analyte and internal standard element and assuming that there are no spectral interferences on the spectral wavelengths chosen. The internal standard elements and the analyte spectral lines should also be integrated at the same time.

References

1 T. Hirasawa, K. Sasaki, M. Taguchi and H. Kaneko, *J. Power Sources*, 2000, **85**, 44.
2 V. Danel and V. Plichon, *Electrochim. Acta*, 1983, **28**, 785.
3 J. A. Borowiec, A. W. Boorn, J. H. Dillard, M. S. Cresse, R. F. Browner and M. J. Matteson, *Anal. Chem.*, 1980, **52**, 1054.
4 H. Kornahrens, K. D. Cook and D. W. Armstrong, *Anal. Chem.*, 1982, **54**, 1325.
5 R. K. Skogerboe and G. B. Butcher, *Spectrochim. Acta, Part B*, 1985, **40**, 1631.
6 J. Porstendörfer, J. Gebhart and G. Röbig, *J. Aerosol. Sci.*, 1977, **8**, 371.
7 *CRC Handbook of Chemistry and Physics*, eds. R. C. Weast and M. J. Astle, CRC Press, Boca Raton, FL, USA, 1981.
8 A. I. Vogel, *A Textbook of Quantitative Chemical Analysis including Elementary Instrumental Analysis,* Longman, Harlow, Essex , 3rd edn., 1961, p. 370.
9 D. A. Skoog, F. J. Holler and T. A. Nieman, in *Principles of Instrumental Analysis*, Saunders College Publishing, USA, 5th edn., 1998, p. 13.