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The Atomic-absorption Spectrophotometric Determination of Total Aluminium in Steel after its Dissolution in a Pressure Bomb

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A method is described for the determination of 0·001 to 0·14 per cent. of total aluminium in irons and steels, which does not involve fusion of an oxide residue. The iron or steel is completely dissolved by first subjecting it to conventional treatment with acid in an open beaker and then to attack by acid in a PTFE-lined bomb at 200 °C. The oxide residue is completely dissolved by attack in the bomb with hydrochloric acid alone or with a mixture of hydrochloric and hydrofluoric acids, the latter solvent being preferred. Iron(III) is extracted from the solution of steel, 6 M in hydrochloric acid, with isobutyl methyl ketone and aluminium is then extracted from the aqueous phase buffered at pH 4·7 with acetylacetone. The concentration of aluminium in the organic phase is determined by atomic-absorption spectrophotometry with a nitrous oxide - acetylene flame. Good results were obtained for the determination of aluminium in eleven standard irons and steels.

ALUMINIUM in steel exists in acid-soluble forms, which include elemental aluminium, and in forms that are insoluble in boiling acid. These acid-insoluble forms are corundum, α-aluminium oxide, and probably aluminium oxide associated with calcium oxide or silicon dioxide, or both. The small amount of acid-insoluble residue is usually brought into solution by fusion with sodium carbonate or with alkali-metal hydrogen sulphate, and the dissolved melt is combined with the initial solution before the determination of total aluminium.

The dissolution procedure would be improved if the fusion step were eliminated. Ito[1] has shown that many minerals that cannot be completely dissolved by attack with acid in an open beaker can be conveniently dissolved by attack with acid in a PTFE-lined bomb at a temperature of 240 °C. We therefore decided to investigate the possibility of dissolving the oxide, which cannot be dissolved by the usual attack with acid, in a similar bomb without the necessity of filtering off the insoluble residue.

We have found that the normally insoluble oxide is dissolved in a pressure bomb and the results of our study are described in this paper. The total aluminium in the solution from the bomb was determined by atomic-absorption spectrophotometry. The instrument at our disposal was a Unicam SP90, Series 1, atomic-absorption spectrophotometer, for which the concentration of aluminium in aqueous solution that produced 1 per cent. absorption was 3 μg ml^{-1}. As the required method had to have a limit of detection of 0·001 per cent., which corresponds to 0·1 μg ml^{-1} for a 1 per cent. m/V solution of the steel, it was necessary to introduce a concentration step for the aluminium. For mild steels, it should be possible to remove iron, the base element, by solvent extraction of iron(III) into isobutyl methyl ketone from 6 M hydrochloric acid and to evaporate the aqueous phase to a small volume in order to obtain a concentration of aluminium that is suitable for atomic-absorption spectrophotometry. However, it was desirable that the method should also be applicable to stainless steels and it was felt that the most satisfactory approach was to remove the iron(III) from a solution of the steel in 6 M hydrochloric acid with isobutyl methyl ketone and then to extract the aluminium as its neutral trisacetylacetonato complex into acetylacetone from an acetate buffer at pH 4·7. It was known that certain elements would at least partially accompany the aluminium into the organic phase, but all of the chromium(III) and most of the nickel(II) would remain in the aqueous phase.[2]

Treatment of the dissolved steel *plus* the small residue containing aluminium in oxide form with approximately 9 M hydrochloric acid in the PTFE-lined bomb at 200 °C for 2½ hours resulted in complete decomposition of the oxide, and the results of applying such a method to the analysis of ten steels are reported and discussed later in the paper. However, this method suffers from the disadvantage that, on longer treatment in the bomb, a small

proportion of the aluminium, which was completely in solution after $2\frac{1}{2}$ hours of heating, is adsorbed on the small silica precipitate and low results for total aluminium are obtained.

To overcome this problem, further work has been undertaken with a mixture of hydrochloric and hydrofluoric acids. Dissolution of oxide is complete after heating for 2 hours at 200 °C and the silica is retained in solution as fluorosilicic acid. Heating with the mixture of acids for periods in excess of 2 hours had, as expected, no effect on the amount of aluminium that remained in solution. With the mixture of acids it was, however, necessary to remove the hydrofluoric acid from solution by heating the solution with sulphuric acid to fumes of sulphur trioxide before extracting the aluminium into acetylacetone as its acetylacetonate. The presence of fluoride in the aqueous phase inhibits the extraction of trisacetylacetonatoaluminium(III) into the organic phase.

Two methods are therefore described for the determination of 0·001 to 0·14 per cent. of total aluminium in irons and steels.

EXPERIMENTAL

APPARATUS—

A Unicam SP90, Series 1, atomic-absorption spectrophotometer was used with a nitrous oxide - acetylene flame. With scale expansion, a Honeywell 10-mV recorder was used.

The pressure bomb was made of stainless steel and was cylindrical in shape with a screw top. It contained a PTFE liner made from a 150-ml PTFE beaker with a circular PTFE disc serving as a lid. The bomb was almost identical in design with that described by A. Hodkinson and R. H. Jenkins (unpublished work). The capacity of the PTFE liner was 85 ml.

REAGENTS—

Hydrochloric acid, sp. gr. 1·18.
Hydrofluoric acid, 40 per cent. m/m.
Nitric acid, sp. gr. 1·42.
Sulphuric acid, sp. gr. 1·84.
These acids were of analytical-reagent grade.
Sodium hydroxide solution, 3 M *and* 5 M—Dissolve 60 g and 100 g, respectively, of analytical-reagent grade sodium hydroxide pellets in water and dilute the solutions to 500 ml with water.
Acetylacetone—General-purpose reagent. Redistil it before use.
Isobutyl methyl ketone—General-purpose reagent.
Ammonium aluminium sulphate—Analytical-reagent grade.
Iron metal—Specpure quality (Johnson Matthey Chemicals Ltd.).
Other metals and salts used were of analytical-reagent grade or of Specpure quality.
Standard aluminium solution A, approximately 1000 μg ml⁻¹—Dissolve 1·679 g of ammonium aluminium sulphate in water and dilute the solution to 100 ml with water. Determine the true concentration of aluminium in this solution titrimetrically with EDTA.[3] Alternatively, a standard aluminium solution can be made from aluminium metal of Specpure quality.
Standard aluminium solution B, approximately 100 μg ml⁻¹—Dilute 10 ml of solution A to 100 ml with water.
Standard aluminium solution C, approximately 10 μg ml⁻¹—Dilute 10 ml of solution B to 100 ml with water.

METHODS

I. DETERMINATION OF TOTAL ALUMINIUM AFTER DISSOLUTION OF THE STEEL WITH HYDROCHLORIC ACID—

To 1·000 g of steel in a PTFE liner, add 12 ml of concentrated hydrochloric acid followed by 3 ml of concentrated nitric acid and heat the mixture gently to dissolve the steel (Note 1). Evaporate the solution to the first appearance of solid iron(III) chloride.

NOTE 1—

If the alloy contains more than 0·05 per cent. of aluminium (500 μg g⁻¹), take an amount of alloy containing less than 500 μg of aluminium and make it up to 1 g with Specpure iron.

Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution to the first appearance of the solid iron(III) chloride. Repeat this operation. Wash any solution on the upper side of the liner into the bottom with 3 ml of concentrated hydrochloric acid and add a further 5 ml of this acid. Place the liner in the bomb, cover the liner with the PTFE lid and close the bomb by screwing on the stainless-steel lid by hand only. Heat the bomb in an oven at 200 °C for $2\frac{1}{2}$ hours. Remove the bomb from the oven and cool it to room temperature under a tap.

Transfer the contents of the liner to a 150-ml beaker with 10 ml of concentrated hydrochloric acid and evaporate the solution to about 10 ml. Dilute the solution to 50 ml with 6 M hydrochloric acid and transfer the diluted solution into a separating funnel. Remove most of the iron from this aqueous phase by shaking it twice with 25-ml volumes of isobutyl methyl ketone. Discard the organic layers. Transfer the aqueous phase to a 100-ml beaker, evaporate the solution to the first appearance of solid and add 5 ml of water. Adjust the pH of the solution to approximately 1 by adding 3 M sodium hydroxide solution dropwise and then to 4·7 by adding sodium acetate crystals. Dilute the solution to approximately 25 ml with water. Extract the aluminium from this aqueous phase in a separating funnel with two 25-ml portions of acetylacetone. Discard the aqueous phase. Combine the organic phases and evaporate this solution to about 7 ml in a small distillation flask on an oil-bath at 150 to 160 °C. Dilute the solution to 10 ml in a calibrated flask with acetylacetone, spray the solution into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer and use the conditions shown in Table I to determine the flame absorbance. With reference to a suitable calibration graph, determine the concentration of total aluminium in the steel.

TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF ALUMINIUM

Acetylene flow-rate at 1·05 bar/l min^{-1}	3·2
Nitrous oxide flow-rate at 2·1 bar/l min^{-1} ..	5·0
Wavelength for use with aluminium lamp/nm ..	309·3
Slit width/mm	0·03
Lamp current/mA	10
Height of centre of light path above burner/mm ..	7

Prepare a calibration graph corresponding to approximately 0 to 0·05 per cent. of aluminium in an alloy by adding a 1-g amount of Specpure iron to each of six beakers followed by 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution B. Treat these standards in exactly the same way as described above for a steel, but omit the treatment in the PTFE-lined bomb. Determine the flame absorbances of these solutions under the same conditions as those used for the alloys and construct a calibration graph.

II. DETERMINATION OF TOTAL ALUMINIUM AFTER DISSOLUTION OF STEEL WITH HYDROCHLORIC AND HYDROFLUORIC ACIDS—

To 1·000 g of steel in a PTFE liner, add 12 ml of concentrated hydrochloric acid followed by 3 ml of concentrated nitric acid and heat the mixture gently to dissolve the steel (Note 1). Evaporate the solution to the first appearance of solid iron(III) chloride.

Add 10 ml of concentrated hydrochloric acid and re-evaporate the solution to the first appearance of the solid iron(III) chloride. Repeat this operation. Wash any solution on the upper side of the liner into the bottom with 3 ml of concentrated hydrochloric acid, then add 4 ml of concentrated hydrofluoric acid. Place the liner in the bomb, cover the liner with the PTFE lid and close the bomb by screwing on the stainless-steel lid by hand only. Heat the bomb in an oven at 200 °C for at least 2 hours. Remove the bomb from the oven and cool it to room temperature under a tap.

Transfer the contents of the liner to a 150-ml beaker with 10 ml of concentrated hydrochloric acid and evaporate the solution to about 10 ml. Dilute the solution to 50 ml with 6 M hydrochloric acid and transfer the diluted solution into a polypropylene separating funnel. Remove most of the iron from this aqueous phase by shaking it twice with 25-ml volumes of isobutyl methyl ketone. Discard the organic layers. Transfer the solution to a 150-ml

PTFE beaker, add 1·5 ml of concentrated sulphuric acid (Note 2), evaporate the solution to fumes of sulphur trioxide and continue the fuming for 5 minutes with occasional agitation of the beaker. Add 10 ml of water to the cooled beaker and adjust the pH of the solution to approximately 1 by adding 5 M sodium hydroxide solution dropwise and then to 4·7 by adding sodium acetate crystals. Dilute the solution to approximately 25 ml with water. Extract the aluminium from this aqueous phase in a separating funnel with two 25-ml portions of acetylacetone. Discard the aqueous phase. Combine the organic phases and evaporate this solution to about 7 ml in a small distillation flask on an oil-bath at 150 to 160 °C. Dilute the solution to 10 ml in a calibrated flask with acetylacetone, spray the solution into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer and use the conditions shown in Table I to determine the flame absorbance. With reference to a suitable calibration graph, determine the concentration of total aluminium in the steel.

Prepare a calibration graph corresponding to approximately 0 to 0·05 per cent. of aluminium in an alloy by adding a 1-g amount of Specpure iron to each of six beakers followed by 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution B. Treat these standards in exactly the same way as described above for a steel, but omit the treatment in the PTFE-lined bomb. Determine the flame absorbances of these solutions under the same conditions as those used for the alloys and construct a calibration graph.

For the determination of aluminium contents of 0·005 per cent. and below, prepare a calibration graph in the same way by using 0, 1, 2, 3, 4 and 5 ml of standard aluminium solution C and $\times 3$ scale expansion with a 10-mV recorder.

NOTE 2—

    With stainless steels, use 4 ml of concentrated sulphuric acid.

STUDIES ON HEATING TIMES FOR COMPLETE DISSOLUTION OF OXIDE—

The method for the determination of total aluminium after dissolution of the steel with hydrochloric acid alone (Method I) was applied to steels B.C.S. 321 (0·4-g sample) and B.C.S. 330 (1-g sample) with different periods of heating in the bomb at 200 °C. From Fig. 1, it can be seen that complete dissolution of aluminium is achieved after $2\frac{1}{4}$ hours but that low results for total aluminium in both steels are obtained on longer heating. The results of the following experiments indicated that low results were due to the adsorption of dissolved aluminium on to a precipitate of insoluble silicon dioxide on heating for periods in excess of $2\frac{1}{4}$ hours.

The steel that showed the greater adsorption effects (B.C.S. 330) was dissolved by using Method I and heated in the bomb for 4 hours. The solution was then filtered through a Whatman No. 541 filter-paper and the filtrate analysed to determine aluminium by continuing with Method I. The residue and the filter-paper were digested in a mixture of hydrofluoric and hydrochloric acids; the silicon dioxide passed into solution as fluorosilicic acid and released adsorbed aluminium. The solution was then filtered to remove pulped filter-paper, the second filter-paper was washed and 1·5 ml of concentrated sulphuric acid added to the filtrate. The solution was then analysed to determine aluminium, after evaporation to fumes, pH adjustment, extraction and concentration, by atomic-absorption spectrophotometry as in Method II. When the aluminium contents of the first filtrate and residue were added together, the certificate value for aluminium in B.C.S. 330 steel was obtained. A similar method applied to a filter-paper from the same batch as the one used above showed that it contained a negligible amount of aluminium.

It should be noted that the tailing-off effect in Fig. 1 following Method I with hydrochloric acid alone and heating periods in excess of $2\frac{1}{4}$ hours is much less for B.C.S. 321 than for B.C.S. 330 steel. The ratios of aluminium to silicon present in these steels are 1:0·4 and 1:23, respectively, which is a further indication that adsorption of aluminium on silicon dioxide is responsible for the low results after long periods of heating.

It can be seen from Fig. 1 that when B.C.S. 330 steel was heated for various periods of time in the bomb with hydrochloric and hydrofluoric acids according to Method II, a constant aluminium content was produced when the period of heating was 2 hours or longer. This indicates that if silicon dioxide is brought into solution, no aluminium is lost and the length of time of heating in the bomb need not be strictly adhered to provided that it is a minimum of 2 hours.
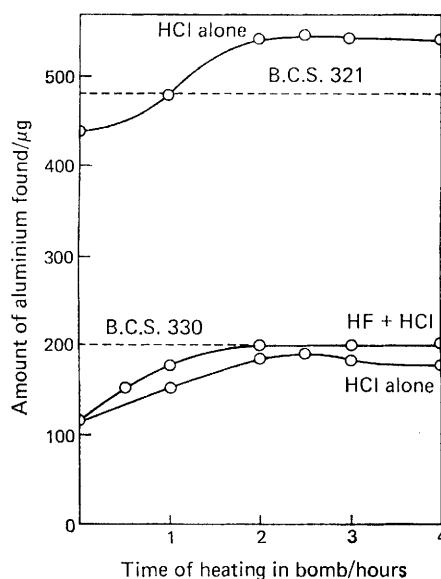
Fig. 1. Effect of time of heating in the bomb on the determination of aluminium in steel. The solid lines correspond to amounts of aluminium found for B.C.S. 321 (0·4-g samples) and B.C.S. 330 (1-g samples) when different acid treatments were used. The upper broken line corresponds to the amount of aluminium expected from the certificate value, which is known only approximately for B.C.S. 321. The lower broken line corresponds to the amount of aluminium expected for B.C.S. 330

TESTS FOR INTERFERING ELEMENTS—

It was appreciated that certain other elements besides aluminium would be partly extracted into the acetylacetone phase when the above methods were used. Various amounts of twenty-four elements, most of which might be present in steels, were subjected to the extraction procedure. These inorganic species were originally present in 25 ml of an aqueous solution that was 0·1 M in both acetic acid and sodium acetate (pH 4·7 buffer). The aqueous solution was shaken with two 25-ml volumes of acetylacetone and the extent of extraction found by determining the amount of each element that remained in the aqueous phase by well established analytical procedures. These were mainly atomic-absorption spectrophotometric methods, but methods that involved absorption spectrophotometry with solutions, gravimetry and titrimetry were also used. The extents of extraction of these elements are shown in Table II.

With the exceptions of iron(III) and aluminium(III), cobalt(II), copper(II), lead(II), manganese(II), molybdenum(VI), nickel(II), niobium(V), tin(IV), titanium(IV), vanadium(V), zinc(II) and zirconium(IV) are each extracted to an extent greater than 5 per cent. However, copper, lead, niobium, tin, titanium, zinc and zirconium are seldom, and in some instances never, present in concentrations greater than 1 per cent. in steel. Cobalt, manganese, molybdenum, nickel and vanadium can be present in greater concentrations, but most of the molybdenum(VI) from a solution of steel would be expected to be extracted into isobutyl methyl ketone from the aqueous 6 M hydrochloric acid solution together with the iron(III).[4] The amount of elements accompanying the aluminium in the final 10 ml of acetylacetone solution is seldom likely to exceed 20 mg, but the possible interfering effects of these elements on the atomic-absorption spectrophotometric determination of aluminium had to be investigated.

TABLE II

EXTENTS OF EXTRACTION OF VARIOUS INORGANIC SPECIES INTO ACETYLACETONE
FROM $0 \cdot 1$ M ACETIC ACID - $0 \cdot 1$ M SODIUM ACETATE SOLUTION

Inorganic species	Extent of extraction, per cent.	Amount originally present in aqueous phase/mg
Aluminium(III)	100	10
Antimony(V)	0	10
Arsenic(V)	0	10
Bismuth(III)	0	10
Boron(III)	4	10
Calcium(II)	0	10
Chromium(III)	0	200
Cobalt(II)	11	100
Copper(II)	96	10
Iron(III)	100	1000
Lead(II)	20	10
Magnesium(II)	0	10
Manganese(II)	7	100
Molybdenum(VI)	84	50
Nickel(II)	10	100
Niobium(V)*	48	20
Phosphorus(V)	0	10
Sulphur(VI)	0	10
Thallium(I)	3	10
Tin(IV)	73	10
Titanium(IV)*	46	10
Vanadium(V)	60	10
Zinc(II)	22	10
Zirconium(IV)	90	10

* The aqueous phase contained a trace amount of fluoride.

This investigation was carried out by replacing x g of a 1-g sample of Specpure iron by x g of another element, where $100x$ is the maximum percentage of the element that is likely to be present in a ferrous alloy, then adding 300 μg of aluminium to the sample and determining the aluminium content of the simulated alloy by Method I. This procedure was applied to the twelve elements mentioned above and the amounts of aluminium found in each instance are shown in Table III. The results indicate that no interfering effects occur. The slight variations from 300 μg are statistical in nature.

TABLE III

RECOVERY OF 300 μg OF ALUMINIUM ADDED TO SAMPLES OF SIMULATED
ALLOYS CONTAINING POSSIBLE INTERFERING ELEMENTS

Element	Amount added/mg	Amount of aluminium found/μg
Cobalt	100	300
Copper	10	300
Lead	3	300
Manganese	100	298
Molybdenum	50	301
Nickel	100	300
Niobium	20	302
Tin	5	299
Titanium	10	303
Vanadium	20	297
Zinc	2	300
Zirconium	5	301

RESULTS FOR THE ANALYSIS OF IRONS AND STEELS

METHOD I (HYDROCHLORIC ACID ALONE)—

The calibration graph for the determination of aluminium in metal samples was a straight line that intersected the absorbance axis at $0 \cdot 002$ absorbance units, which corresponds to an aluminium blank from the reagents of $0 \cdot 4$ μg ml^{-1}. From this calibration graph, the concentration of aluminium that produced 1 per cent. absorption was calculated as $0 \cdot 9$ μg ml^{-1}.

The results for the determination of aluminium in ten British Chemical Standards samples are given in Table IV.

To obtain precision values, six other samples of B.C.S. 260/3 iron were analysed in addition to the four samples for which results are reported in Table IV. The aluminium contents of these six samples were found to be 0·0019, 0·0023, 0·0020, 0·0018, 0·0014 and 0·0025 per cent. The average of the ten results was 0·0019 per cent. with a standard deviation from the mean of 0·000 36 per cent. The limit of detection of the method is, therefore, 0·0007 per cent.

TABLE IV

ALUMINIUM CONTENTS OF METAL SAMPLES DETERMINED BY METHOD I

The results were obtained on the Unicam SP90 spectrophotometer without scale expansion

Alloy		Aluminium content determined by Method I, per cent.	Average aluminium content by Method I, per cent.	Certificate value, per cent.
B.C.S. No.	Type			
149/3	High-purity iron	0·0039, 0·0031, 0·0030, 0·0036	0·0034	< ∼0·003
260/3	High-purity iron	0·0020, 0·0017, 0·0014, 0·0016	0·0017	∼0·001
320	Mild steel	0·0143, 0·0136, 0·0138, 0·0137	0·0139	0·013
321	Mild steel	0·124, 0·141, 0·139, 0·145	0·137	∼0·12
322	Mild steel	0·0921, 0·0942, 0·0939, 0·0953	0·0939	0·093
325	Mild steel	0·0276, 0·0277, 0·0293, 0·0278	0·0281	0·028
328	Mild steel	0·0479, 0·0482, 0·0485, 0·0489	0·0484	0·050
329	Mild steel	0·0574, 0·0590, 0·0584, 0·0581	0·0582	0·058
330	Mild steel	0·0194, 0·0197, 0·0199, 0·0192	0·0196	0·020
224/1	Cr - V steel	0·0054, 0·0045, 0·0043, 0·0060	0·0051	∼0·005

METHOD II (HYDROCHLORIC AND HYDROFLUORIC ACIDS)—

The calibration graph for the determination of more than 0·005 per cent. of aluminium in mild and low-alloy steels was a straight line that intersected the absorbance axis at 0·005 absorbance unit, which corresponds to an aluminium blank for the reagents of 1·3 μg ml^{-1}. A similar graph was obtained for stainless steels, but the reagent blank was 3·0 μg ml^{-1}.

The calibration graph for the determination of less than 0·005 per cent. of aluminium in high-purity irons was a straight line. As expected, the aluminium blank for the reagents was 1·3 μg ml^{-1}, as for the mild steels.

The results for the determination of aluminium in eleven British Chemical Standards samples are given in Table V.

To obtain precision values, six other samples of B.C.S. 260/3 iron were analysed in addition to the four samples for which results are reported in Table V. The aluminium contents of these six samples (obtained by using ×3 scale expansion and a recorder) were found to be 0·0019, 0·0016, 0·0016, 0·0017, 0·0017 and 0·0019 per cent. The average of

TABLE V

ALUMINIUM CONTENTS OF METAL SAMPLES DETERMINED BY METHOD II

The results were obtained on the Unicam SP90 spectrophotometer without scale expansion, except those marked with an asterisk

Alloy		Aluminium content determined by Method II, per cent.	Average aluminium content by Method II, per cent.	Certificate value, per cent.
B.C.S. No.	Type			
149/3	High-purity iron	0·0031,* 0·0032,* 0·0034,* 0·0033*	0·0033	< ∼0·003
260/3	High-purity iron	0·0016,* 0·0018,* 0·0017,* 0·0016*	0·0017	∼0·001
320	Mild steel	0·0134, 0·0137, 0·0140, 0·0135	0·0137	0·013
321	Mild steel	0·136, 0·138, 0·134, 0·131	0·135	∼0·12
322	Mild steel	0·0937, 0·0931, 0·0941, 0·0934	0·0936	0·093
325	Mild steel	0·0272, 0·0289, 0·0294, 0·0280	0·0284	0·028
328	Mild steel	0·0495, 0·0512, 0·0520, 0·0490	0·0504	0·050
329	Mild steel	0·0581, 0·0578, 0·0580, 0·0584	0·0581	0·058
330	Mild steel	0·0211, 0·0200, 0·0196, 0·0197	0·0201	0·020
224/1	Cr - V steel	0·0052, 0·0051, 0·0052, 0·0050	0·0051	∼0·005
235/2	Stainless steel + Ti	0·0478, 0·0486, 0·0480, 0·0481	0·0481	∼0·048

* Results obtained by using ×3 scale expansion and a recorder.

the ten results was 0·0017 per cent. with a standard deviation from the mean of 0·000 12 per cent.   The limit of detection of the method is, therefore, 0·0002 per cent.

Discussion

The results obtained by both methods are considered to be satisfactory.   However, unless the silicon content of the steel is less than 0·1 per cent., Method II, involving dissolution of aluminium-containing oxides with hydrochloric and hydrofluoric acids, is recommended because careful control of the period of heating in the pressure bomb is unnecessary provided that it is not less than 2 hours.   If results of the highest precision are not required, the flame absorbances can be read on the meter without scale expansion.   However, the use of ×3 scale expansion and a recorder for absorbance measurements leads to a significant increase in precision, the limit of detection (twice the standard deviation of ten determinations near the blank level) being 2 μg g^{-1} by this procedure compared with 7 μg g^{-1} by visual inspection of the meter.

For 1-g samples of many mild steels, in which the concentration of aluminium is in excess of 0·005 per cent., the second solvent extraction could be eliminated and the aqueous iron-free solution could be adjusted to a volume of 10 ml before spraying it into the nitrous oxide - acetylene flame of the atomic-absorption spectrophotometer.   With stainless steels, the first extraction does not remove chromium(III) and nickel(II) from a 6 M solution of the steel in hydrochloric acid and the double extraction procedure is recommended.   When precise results are required for irons or steels containing less than 0·005 per cent. of aluminium, a double extraction procedure is beneficial as a determination of aluminium is three times more sensitive when an acetylacetone solution rather than an aqueous solution is sprayed. Any type of PTFE-lined bomb that will withstand the high pressures produced by heating at 200 °C will be suitable for the dissolution of the aluminium-containing oxides in steel.

References

1.   Ito, J., *Bull. Chem. Soc. Japan*, 1962, **35**, 225.
2.   Starý, J., "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford, 1964, p. 51.
3.   Vogel, A. I., "A Text-Book of Quantitative Inorganic Analysis," Third Edition, Longmans, Green and Co., London, 1962, p. 436.
4.   Swift, E. H., *J. Amer. Chem. Soc.*, 1924, **46**, 2378.