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Gas-Chromatographic Separation of Inorganic Chlorides and Its Application to Metal Analysis. III. Determination of Silicon and Tin in Nonferrous Alloys

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Gas-Chromatographic Separation of Inorganic Chlorides and Its Application to Metal Analysis.

III. Determination of Silicon and Tin in Nonferrous Alloys

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Summary

In this paper gas-chromatographic techniques are described for the determination of silicon in nickel, copper, and aluminum alloys. The methods are similar to that developed earlier for silicon analysis in iron and steel, comprising essentially a conversion of the alloy with gaseous chlorine followed by gas-chromatographic analysis of the volatile chlorides formed.

An analogous but somewhat simpler procedure has been studied for the determination of tin in common tin-containing alloys, such as solders, bearing alloys, type metals, and low-melting alloys.

The gas-chromatographic techniques are rapid and are carried out on the milligram scale. Analysis time is of the order of 15 min. Standard deviations are between 0.01 and 0.03% for silicon determination on a level of 0.7%. For tin determination on a level of 10%, a standard deviation of about 0.2% is found. The analyses require very few manipulations.

The destruction of metals by gaseous chlorine proves to be fast and complete, even for corrosion-resistant alloys such as Monel and Hastelloy.

INTRODUCTION

In previous publications the quantitative analysis was described of volatile metal chlorides by gas chromatography and the application of this procedure to the determination of silicon in iron and steel (*1*,*2*). It was shown that the reaction of gaseous chlorine with the heated metal sample produced silicon tetrachloride in stoichiometric amounts, thus constituting the basis for a rapid and accurate method for silicon analysis in iron and steel.

The present article deals with a few more analogous applications of gas chromatography, specifically in the field of nonferrous alloys. The determination of two elements is considered, namely, silicon and tin.

EXPERIMENTAL

Outline of Methods

The conversion of metal into the corresponding chlorides and the subsequent gas-chromatographic analysis were carried out in two ways, viz., by a direct and an indirect method.

Direct Method. The sample is introduced into a small heated quartz tube upstream of the gas-chromatographic column. By means of a gas-sampling system, a discrete volume of chlorine gas is passed into the carrier gas stream. The volatile chlorides are swept into the column by the carrier gas as soon as they are formed.

Indirect Method. The metal sample is brought into a small heated quartz tube which is connected to a trapping column. Conversion of the metal is effected by a continuous stream of chlorine gas passing over it. The volatile chlorides are collected in the trapping column, while the excess of chlorine is vented. Subsequently, the trapping column is included into the chromatographic circuit. By applying some heat, the chlorides are desorbed from the trapping column, whereupon the gas-chromatographic analysis proceeds as usual.

The direct procedure is indicated when major components of alloys have to be determined. Since small samples are involved (of the order of 1 mg), only a small volume of chlorine gas is required, e.g., about 10 ml. The indirect technique permits the use of more chlorine and is, therefore, more suitable for examining larger alloy samples for minor constituents.

The indirect technique, as used for the determination of silicon in iron and steel, has been described in detail in a previous paper (2).

Apparatus

The apparatus used in the direct procedure is shown in Fig. 1. Nitrogen is used as the carrier gas. In addition to means for drying, adjusting, and measuring the carrier and reference gas stream (1 to 8, 15 to 18), the apparatus comprises a chlorine introduction system (12, cocks A and B), a chlorination tube (11), the chromatographic column (13), and the detector (14).

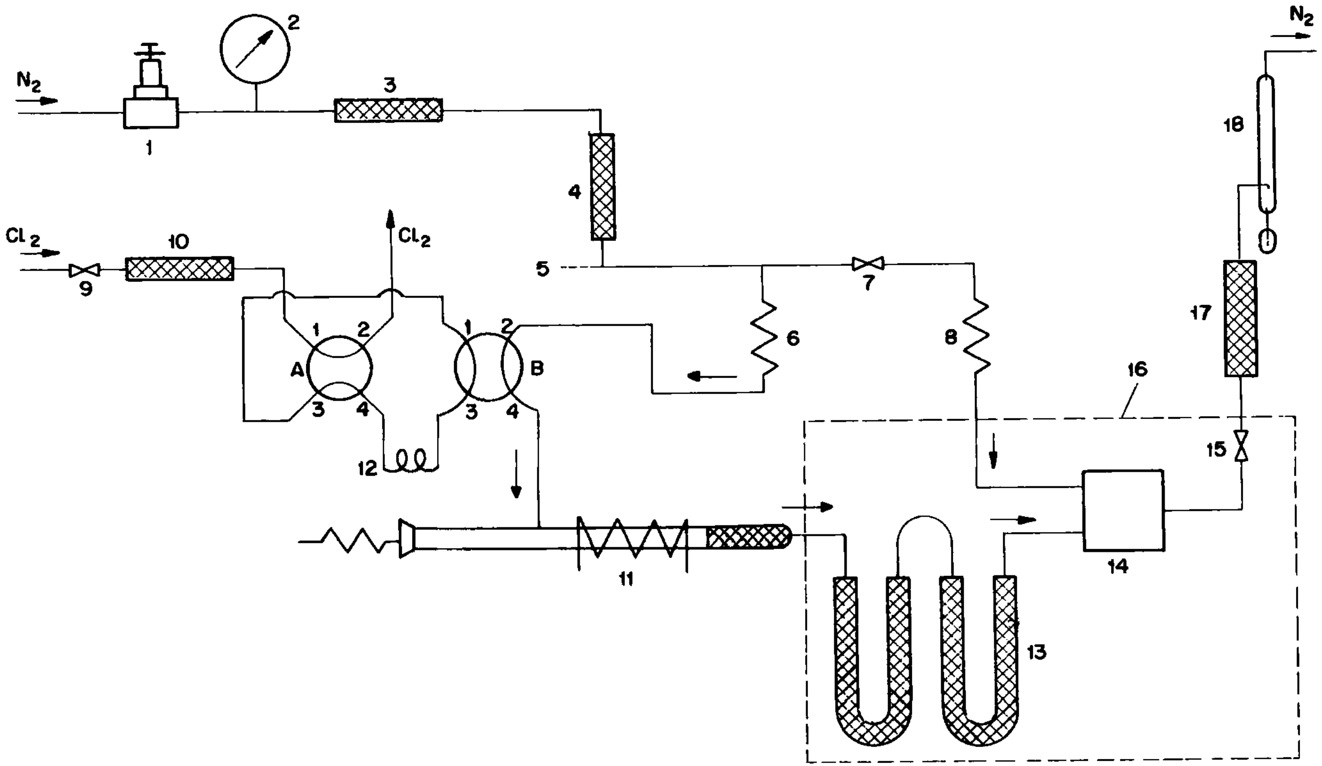

FIG. 1. Flow scheme of apparatus used in direct technique. 1, Precision reducing valve; 2, precision manometer; 3, molecular sieves drier; 4, phosphorus pentoxide drier; 5, connection to be used in indirect technique; 6, capillary restriction; 7, needle valve; 8, capillary restriction; 9, needle valve; 10, phosphorus pentoxide drier; 11, chlorination tube; 12, gas sampling system; 13, chromatographic column; 14, gas density detector; 15, needle valve; 16, air thermostat; 17, absorption tower with KOH; 18, soap film flowmeter.

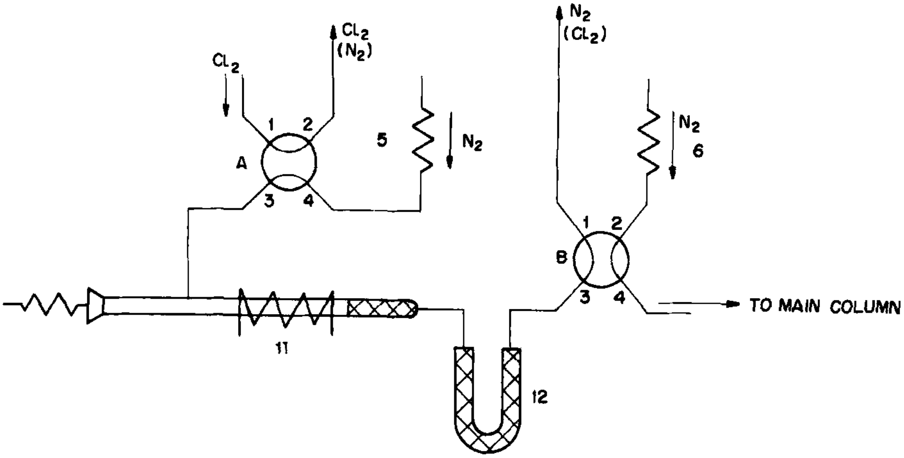

FIG. 2. Modification of apparatus for indirect technique. 5, Capillary restriction; 12, trapping column. Other figures correspond to those in Fig. 1.

The chromatographic column is a glass tube (200 × 0.8 cm i.d.) filled with Kel F-40 polymer wax* (15 wt. %) on Haloport-F† (30–80 mesh). The detector used is a gas density detector constructed from Monel.‡

The chlorination tube is made of quartz. The central part of the tube (1-cm i.d.) can be heated to a temperature of up to 1000°C by means of an electric heater consisting of windings of bare nichrome ribbon fed from a low-voltage transformer. Samples are weighed on a microbalance and are kept in a sample boat in the unheated part of the chlorination tube prior to analysis. The sample boat can be introduced into the hot section by manipulation with a magnet from the outside. The colder downstream part of the tube is loosely filled with quartz wool (serving to retain solid deposits of heavier chlorides) and is connected to the chromatographic column via a heated capillary.

The apparatus used in the indirect technique consists mainly of the same components, but in a slightly different arrangement (Fig. 2). An extra part is the trapping column (a glass tube 30 cm long and 8-mm i.d., filled with the same material as the chromato-

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* Minnesota Mining and Manufacturing Co., St. Paul, Minn.

† F & M Scientific Co., Avondale, Pa.

‡ Gow-Mac Instrument Co., Madison, N.J.

graphic column). With the inlet of the trapping column connected to the chlorination tube and the outlet to the atmosphere, either chlorine gas or nitrogen can be passed through (conditions prevailing during the "chlorination" and "purging" steps, respectively). Cock B (Fig. 2) permits the trapping column to be connected to the main column which can then receive the volatile chlorides collected.

A detailed description of the apparatus as used in the indirect technique has been given previously (2).

RESULTS AND DISCUSSION

Determination of Silicon in Nickel and Copper Alloys

The procedure adopted is essentially the same as described previously for iron and steel samples (2). However, it was found to be advantageous to use a somewhat higher chlorination temperature to facilitate volatilization of the main products of chlorination, which have low volatilities [$NiCl_2$, sublimation point 987°C (3); and $CuCl_2$, bp 954–1032°C (4)].

The analyses were carried out under the following conditions:

Sample size: up to 40 mg of alloy (filings or turnings)
Furnace temperature: 900°C
Chlorination: 2–4 min with 1–2 liters/hr of chloride
Purging: 1 min with 3 liters/hr of nitrogen
Temperature of trapping column: 0–5°C during absorption; 90–100°C during desorption
Temperature of analysis column: 75°C
Carrier gas flow rate: between 2 and 2.5 liters/hr (at 20°C)
Reference gas flow rate: between 3 and 4 liters/hr (at 20°C)

All metal samples examined (including several samples known for their resistance against attack by halogens, such as Hastelloy, Inconel, and Monel) proved to be readily and quantitatively convertible. No problems were met with nickel alloys having a low copper content, the analysis proceeding as smoothly as in the case of iron and steel samples. However, a slight complication arose with materials rich in copper, such as bronze, cupro nickel, or Monel. In these cases we found that the chlorine peak tailed more than usual, which detracted from the accuracy of the determination (see Fig. 3A). This phenomenon is probably caused by dissociation of molten cupric chloride [mp 498°C (*4*)] deposited in relatively hot parts of the chlorination tube. It is known (*4*) that the reaction of copper with excess chlorine yields $CuCl_2$ in addition to CuCl, while heating $CuCl_2$ to above 344°C in an inert atmosphere leads to the formation of chlorine and CuCl. Thus, after the chlorination proper, some chlorine is slowly given off to the nitrogen stream flowing through the chlorination tube.

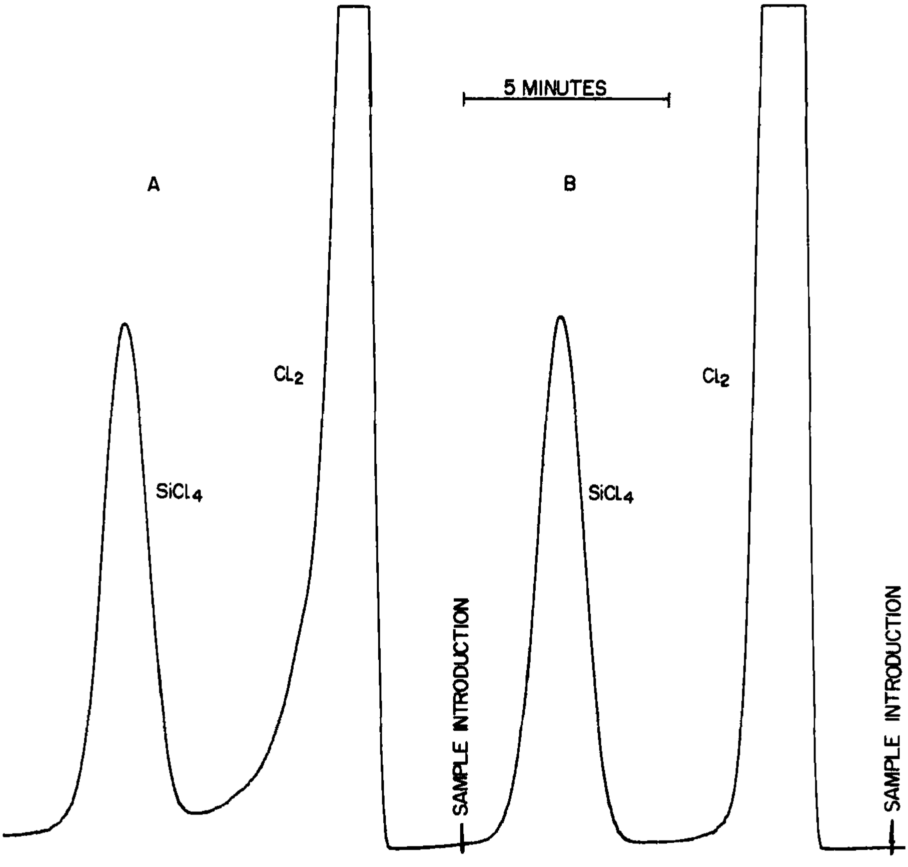

FIG. 3. Determination of silicon in an alloy rich in copper. A, Chromatogram of 22.58 mg of Monel containing 0.67 wt. % Si. Heater of chlorination tube kept on throughout analysis. Note the tailing of the chlorine peak. B, Chromatogram of 24.43 mg of the same alloy. Heater switched off after the chlorination. Note the improvement of the chlorine peak shape.

In agreement with the above we found that an improvement was obtained by switching off the heater just after the chlorination step (see Fig. 3B). This intermittent use of the heater presents no problems since the time constant of the bare nichrome ribbon windings is very small.

As shown in Fig. 4, a proportional relationship exists between the sample size and the areas of the silicon tetrachloride peaks for a given sample. The absence of a blank value was proved on pure nickel, which did not produce a detectable silicon tetrachloride peak (i.e., Si content below 50 ppmw).

Table 1 presents some results obtained for a number of nickel and copper alloys. For these analyses the apparatus had been calibrated by means of a steel sample of known silicon content (British Chemical Standards 255, Si content 0.625 wt. %). It can be seen that the results of the gas-chromatographic analyses are in satisfactory agreement with the values obtained by classical wet analysis. The precision appears to be about the same as found earlier for iron and steel samples.

Determination of Silicon in Aluminium Alloys

In view of the relatively low silicon content of most alloys of interest, we applied the indirect procedure, as worked out for iron and steel samples (2). However, in preliminary experiments with a quartz sample boat, we obtained high and erratic figures. For an aluminium alloy containing 0.7 wt. % Si, deviations ran as high as 50% relative. Whereas no detectable $SiCl_4$ peak was found on analyzing spectroscopically pure iron, a pronounced peak was obtained with pure (about 15 ppmw Si) aluminium. Examination of the quartz boats after analyzing aluminium samples gave evidence of attack by molten metal. Evidently some SiO_2 is reduced to the element which yields $SiCl_4$ with chlorine vapor. It is known (5) that silicon can be prepared from SiO_2 by a thermite reaction: Upon ignition of a mixture of sand, sulfur, and excess aluminium powder, aluminium sulfide forms with evolution of heat, which brings the mixture to a temperature where SiO_2 is reduced by the remaining Al. Since the reaction of aluminium with chlorine is also highly exothermic, the sample in the present procedure can reach temperatures far above that of the oven tube during chlorination.

In agreement herewith, the use of graphite or alumina as ma-

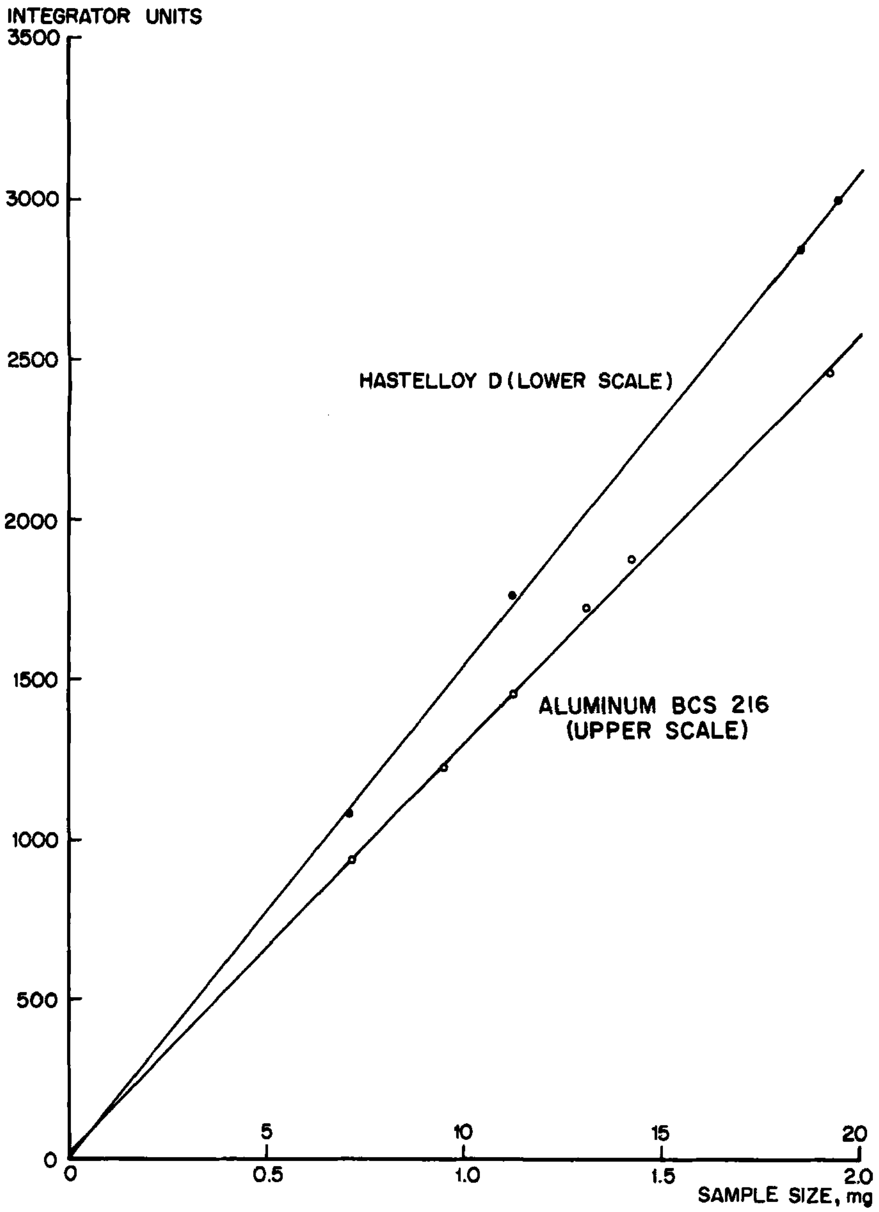

FIG. 4. Linearity of response in silicon determination.

TABLE 1

Determination of Silicon in Nickel and Copper Alloys[a]

Sample	Composition, wt. %[b]	Weight range, mg	Number of determinations	Si, wt. %		Maximum deviation from mean, wt. %	Deviation from known value, wt. %
				Known value	Mean found		
Hastelloy B	64.4 Ni, 27.5 Mo, 5.6 Fe, 0.4 V, 0.7 Mn	12–17	2	0.21	0.225	0.005	0.015
Hastelloy C	55.6 Ni, 16.1 Cr, 14.3 Mo, 6.0 Fe, 3.6 W, 0.5 Mn	11–18	2	0.79	0.785	0.005	−0.005
Hastelloy D	84.4 Ni, 3.8 Cu, 0.5 Fe, 0.4 Al	0.7–1.9	4	9.1	8.90	0.10	−0.2
Carpenter 20 Cb	46 Fe, 28.2 Ni, 20.4 Cr, 2.5 Mo, 2.1 Cu, 1.0 Mn, 0.4 Cb + Ta	12–24	2	0.70	0.695	0.005	−0.005
Inconel	77.0 Ni, 15.0 Cr, 7.0 Fe, 0.3 Mn, 0.1 Cu	20–23	3	0.46	0.480	0.000	0.02
Monel NBS 162	66.4 Ni, 28.9 Cu, 2.3 Mn, 0.5 Co, 0.3 Fe, 0.2 Cr, 0.2 Al, 0.2 Ti	16–25	3	0.67	0.653	0.007	−0.017
Cupro nickel BCS Cu/Ni "A"	68.8 Cu, 30.1 Ni, 0.9 Mn	30–42	2	0.12	0.122	0.002	0.002
Silicon bronze	95.7 Cu, 0.7 Mn	3.7–6.1	2	3.2	3.13	0.03	−0.07

[a] NBS, National Bureau of Standards; BCS, British Chemical Standards.
[b] Elements present in concentrations below 0.1 wt. % not reported.

terials for the sample boat gave improved results. However, the blank value was still quite considerable and the results were still systematically high (by anything up to 10% relative). We suspect, therefore, that some additional $SiCl_4$ is formed by the reaction of Al_2Cl_6 with the hot inner surface of the quartz tube. Although we could find no support for such a reaction in the literature, a thermodynamic calculation of the equilibria

$$3SiO_{2_{\text{vitreous}}} + 2Al_2Cl_{6_{\text{solid}}} \rightleftharpoons 3SiCl_{4_{\text{vapor}}} + 2Al_2O_{3_{\text{solid }\alpha}}$$

and

$$3SiO_{2_{\text{vitreous}}} + 2Al_2Cl_{6_{\text{vapor, 1 atm}}} \rightleftharpoons 3SiCl_{4_{\text{vapor}}} + 2Al_2O_{3_{\text{solid }\alpha}}$$

from standard free energies (3) and heat capacity data (6–8) at the temperatures involved showed that the amount of $SiCl_4$ which can be formed in theory amply accounts for the quantity found.

An obvious way of eliminating the above trouble is to keep the rate of $SiCl_4$ formation low by keeping the quartz surface cool. This may be effected by employing an inductive or infrared means of heating with, e.g., a graphite sample boat. However, it was found that the same goal could be reached with only minor alterations in the existing apparatus, viz., by inserting a sintered-alumina (corundum) tube into the (slightly modified) quartz tube (Fig. 5), as a result of which the hot quartz surface was shielded from the reaction vapors. Thus the blank value is reduced to about 100 ppmw Si for a 20-mg sample (with a graphite or alumina boat).

At 600–900°C a number of representative aluminium alloys were

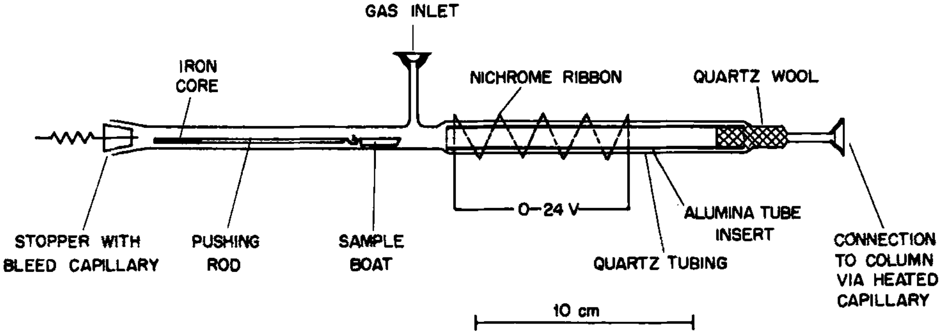

FIG. 5. Chlorination tube with alumina insert for analysis of aluminium alloys.

TABLE 2

Determination of Silicon in Aluminium Alloys[a]

Sample	Composition, wt. %[b]	Weight range, mg	Number of determinations	Si, wt. %		Maximum deviation from mean, wt. %	Deviation from known value, wt. %
				Known value	Mean found		
Aluminium alloy BCS 216	4.2 Cu, 0.8 Fe, 0.5 Mn, 0.5 Mg, 0.3 Zn, 0.2 Ni	12–17	6	0.71	0.73	0.02	0.02
Aluminium alloy BCS 263	4.2 Mg, 0.5 Mn, 0.4 Fe, 0.3 Cr, 0.1 Cu	22–36	3	0.14	0.17	0.03	0.03
Aluminium alloy BCS 262	10.6 Mg, 0.2 Fe, 0.1 Ti	20–26	2	0.10	0.10	0.01	0.00
Sheet aluminium 26 SW	4.6 Cu, 0.8 Mn, 0.7 Mg, 0.4 Fe	13–17	10	0.72	0.69	0.05	−0.03
Casting alloy Nedal 25	1.3 Cu, 0.5 Mg	2.2–2.8	3	5.19	5.03	0.13	−0.16
Aluminium 2 S	0.2 Fe	32–43	3	0.12	0.11	0.01	−0.01
Noral Alloy M 575	2.2 Mg, 0.4 Fe, 0.3 Mn	20–27	4	0.25	0.24	0.03	−0.01
Silumin	0.2 Fe	0.6–0.9	3	12.1	12.2	0.5	0.1

[a] BCS, British Chemical Standards.

[b] Al, balance. Elements present in concentrations below 0.1 wt. % not reported.

chlorinated. No difficulties were experienced in the complete destruction of metal samples up to 40 mg (consisting mainly of turnings), except when magnesium was present in concentrations of about 5 wt. % or higher. In the latter case, $MgCl_2$ [mp 714°C; bp 1418°C (3)] was not volatilized and the conversion of metal was retarded. By mixing the sample with graphite powder, an improvement was obtained (probably because the formation of a continuous thick layer of molten salt was avoided), and it was found that magnesium-containing alloys could be converted at 900°C in less than 10 min.

Figure 4 shows that the linearity of detector response is also satisfactory for aluminium samples.

Some results obtained on a number of aluminium alloys are collected in Table 2. With the exception of the chlorination conditions already discussed, the analytical parameters are the same as mentioned in the preceding part. Calibration of the apparatus was also carried out with a standard steel sample.

Data on the repeatability of the method are given in Table 3. From these figures it can be concluded that the present gas-chro-

TABLE 3

Repeatability of Gas-Chromatographic Determination of Silicon in Aluminium Alloys[a]

Determination no.	Si found, wt. %
1	0.651
2	0.658
3	0.679
4	0.736
5	0.708
6	0.670
7	0.670
8	0.703
9	0.705
10	0.716
Mean value found	0.690
Maximum deviation from mean	0.046
Standard deviation	0.026

[a] Samples: 13–17 mg of aluminium filings reported to contain 0.72 wt. % Si.

matographic method is less accurate than the corresponding method for steel samples (2) (standard deviations on a 0.7 wt. % level about 0.03 and 0.008%, respectively). Nevertheless, the accuracy of the gas-chromatographic method for silicon determination in aluminium alloys is not much inferior to that of existing wet chemical methods. For example, for the classical Regelsberger method (which is generally regarded as the most accurate gravimetric method) an accuracy of 0.01–0.03% is reported for 0.1–1% silicon (9).

Determination of Tin

Since in the more important tin-containing alloys (e.g., bronzes, babbits, solders, type metals, low-melting alloys, etc.) this element is a major constituent, we applied the direct technique. The following conditions were adopted:

Sample size: up to 10 mg (usually 1–2 mg)
Volume of chlorine gas: 10 ml
Temperature of chlorination tube: 600°C
Temperature of analysis column: 100°C
Carrier gas flow rate: between 2 and 2.5 liters/hr (at 20°C)
Reference gas flow rate: between 3 and 4 liters/hr (at 20°C)

In addition to a number of previously analyzed alloys which were available, we also examined a few simple binary alloys (lead–tin and antimony–tin), prepared by fusing together accurately weighed amounts of the pure metals in a nitrogen atmosphere. The homogeneous melts were rapidly frozen to avoid segregation during solidification.

The conversion of the metal into chlorides was quantitative in all cases examined. This follows from the visual absence of any unconverted metal residue, as well as from the fact that repeated injections of chlorine failed to give additional $SnCl_4$ in detectable quantities.

Figure 6 is a typical chromatogram obtained with the present technique. Figure 7 illustrates the proportional relationship between the area of the tin tetrachloride peak and the weight of the sample.

Some results obtained on several alloys are presented in Table 4. For these analyses the apparatus had been calibrated with a lead–

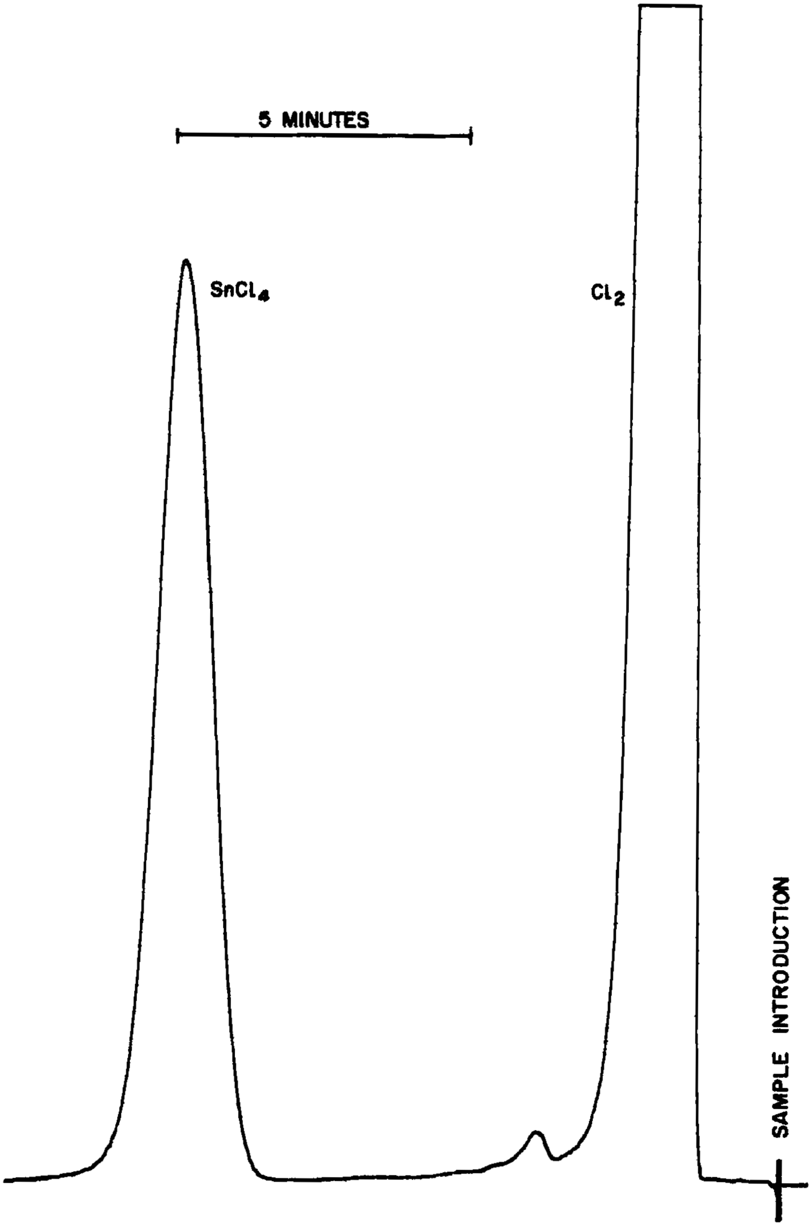

FIG. 6. Chromatogram of a tin-containing alloy. Sample, 1.66 mg of Rose metal (22.9 wt. % Sn); column temperature, 100°C.

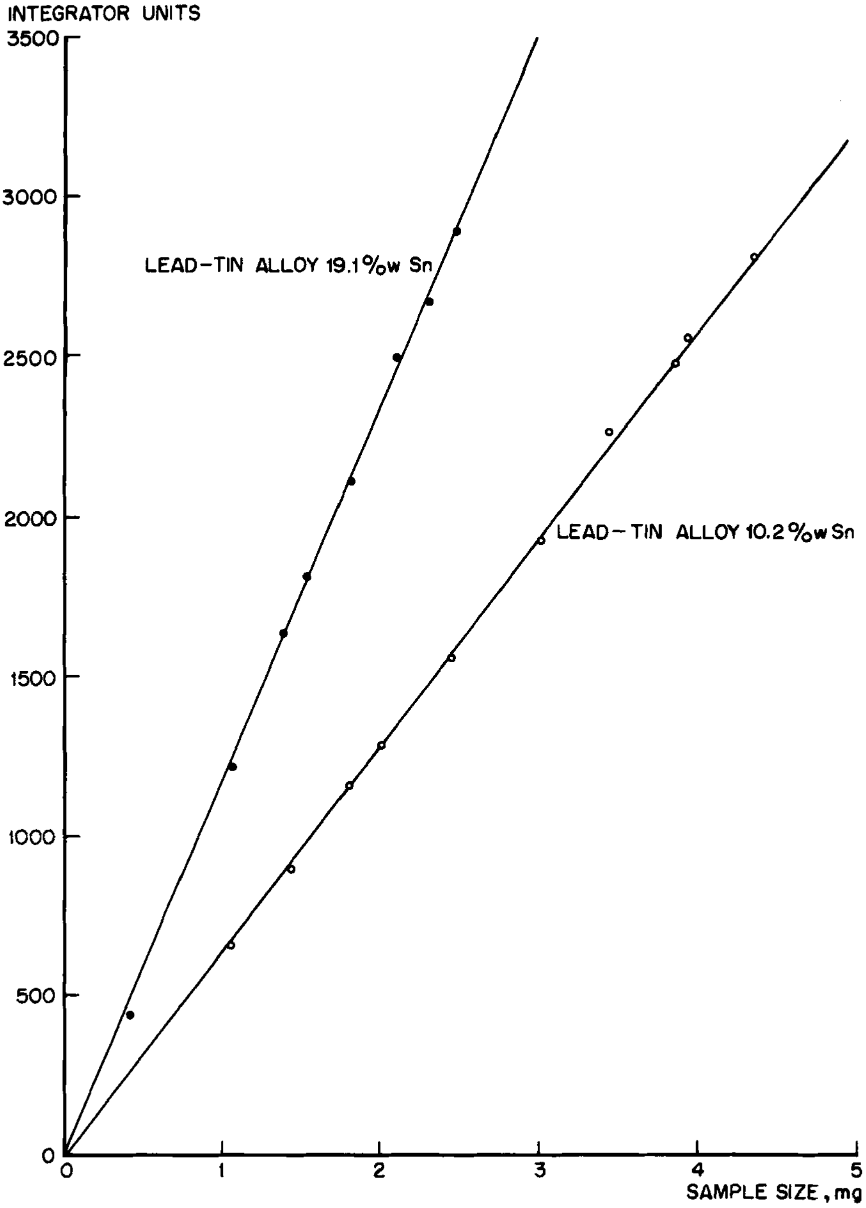

FIG. 7. Linearity of response in tin determination.

TABLE 4

Determination of Tin in Various Alloys

Sample	Composition, wt. %[a]	Weight range, mg	Number of determinations	Sn, wt. %		Maximum deviation from mean, wt. %	Deviation from known value, wt. %
				Known value	Mean found		
Lead–tin alloy (soft solder)	40.0 Pb	0.6–1.1	3	60.0	58.9	0.6	−1.1
Lead–tin alloy	79.9 Pb	1.4–2.3	3	20.1	19.7	0.2	−0.4
Lead–tin alloy	89.9 Pb	1.4–4.3	4	10.2	10.0	0.4	−0.2
Lead–tin alloy	94.9 Pb	5.7–9.6	3	5.19	5.13	0.06	−0.06
Antimony–tin alloy	79.7 Sb	1.3–1.7	3	20.3	20.4	0.3	0.1
Bronze	93.8 Cu, 0.1 Zn	2.2–4.4	5	5.8	6.4	0.3	0.6
Bronze, SAE 62	87.4 Cu, 0.3 Zn	1.8–2.9	3	12.3	12.1	0.2	−0.2
Woods metal	50 Bi, 25 Pb, 13 Cd	1.9–3.8	4	11.2	11.6	0.4	0.4
Rose metal	50.0 Bi, 27.1 Pb	1.0–1.9	3	22.9	23.5	0.3	0.6

[a] Elements present in concentrations below 0.1 wt. % not reported.

TABLE 5

Repeatability of Gas-Chromatographic Determination of Tin[a]

Determination no.	Sn found, wt. %
1	10.60
2	10.32
3	10.18
4	10.45
5	10.76
6	10.47
7	10.36
8	10.51
9	10.24
10	10.47
11	10.48
Mean value found	10.44
Maximum deviation from mean	0.32
Standard deviation	0.17

[a] Samples: 1.0–6.0 mg of a lead–tin alloy containing 10.2 wt. % Sn.

tin alloy of accurately known composition. In general, agreement with established values is satisfactory.

Table 5 presents some results of a series of analyses carried out to assess the precision of the gas-chromatographic method. From these data a coefficient of variation of 1.6% is calculated.

Under the conditions stated above, the time required for an analysis is 15–20 min (including weighing of the sample, but excluding periodic calibration of the apparatus). It is easy, however, to reduce the analysis time to about 10 min or even less, for instance, by raising the column temperature (see Fig. 8).

CONCLUDING REMARKS

The present study shows that the gas-chromatographic procedure worked out earlier for the determination of silicon in iron and steel is also applicable to nonferrous alloys with only minor modifications. As discussed before in relation to iron and steel analysis (2), gas-chromatographic techniques offer important advantages over classical wet chemical methods, such as short analysis time, sensitivity, simplicity of operation, and adaptability to automation.

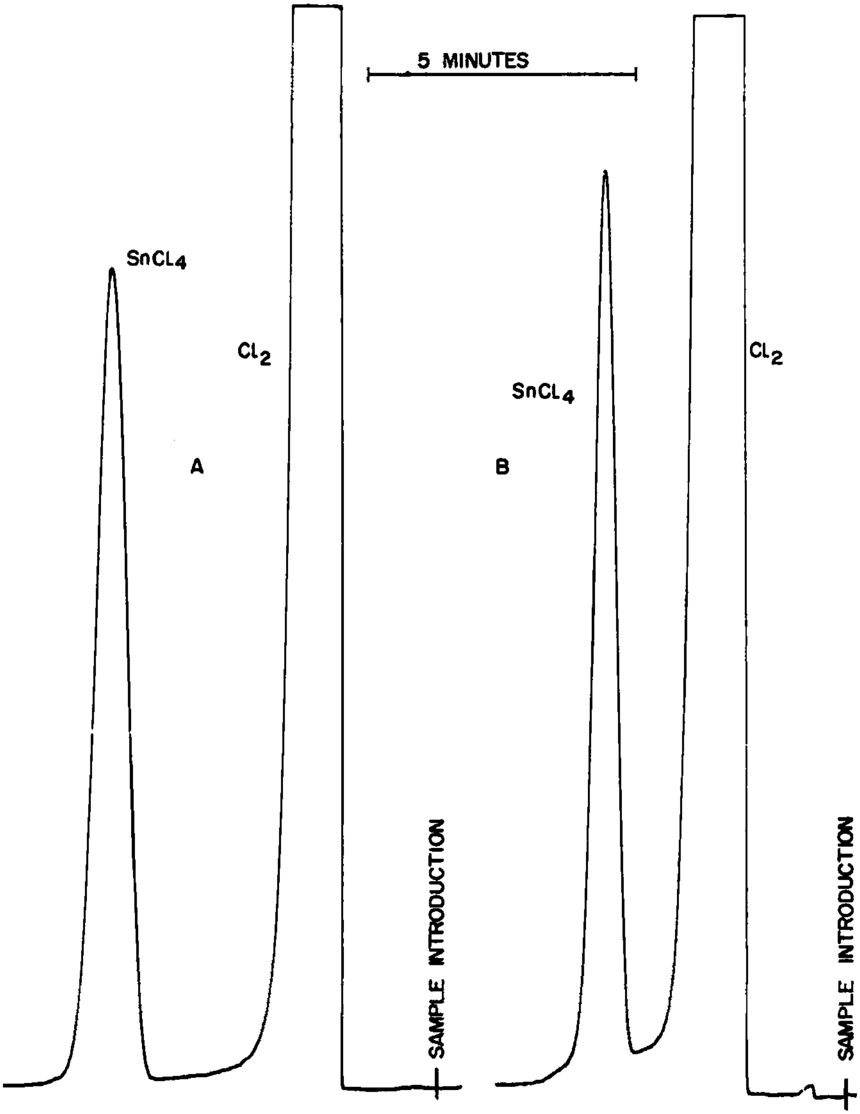

FIG. 8. Effect of temperature on speed of tin determination. A, 0.48 mg of Sn; column temperature, 125°C. B, 0.32 mg of Sn; column temperature, 150°C. $SnCl_4$ peak attenuated by a factor of 2 in both chromatograms.

As regards rapidity, there is a considerable difference between the classical methods of silicon determination in aluminium and the present one. A gas-chromatographic analysis can be completed in about 15 min, whereas the classical Regelsberger method takes about 3 hr (*10*) and involves numerous manipulative steps. Even the more rapid Fuchshuber method still takes about 1½ hr (*10*).

The simplicity of the gas-chromatographic method is particularly well illustrated by the direct method, as exemplified by the determination of tin. Here manipulation consists only of weighing and introducing the sample, followed by turning the cocks for the chlorine gas introduction.

Another feature of the gas-chromatographic method is its versatility with respect to sample type. The conversion of metals into chlorides has been shown to be rapid and complete. This is even true of Hastelloy C and Monel, which are among alloys known for their resistance against attack by halogen vapors.

REFERENCES

1. S. T. Sie, J. P. A. Bleumer, and G. W. A. Rijnders, *Separation Sci.*, **1**, 41 (1966).
2. S. T. Sie, J. P. A. Bleumer, and G. W. A. Rijnders, *Separation Sci.*, **2**, 645 (1967).
3. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Nat. Bur. Std. Circ.*, **500** (1952).
4. P. Pascal, *Nouveau traite de chimie minerale*, T. III, Masson et Cie, Paris, 1957, pp. 242–249.
5. G. Fowles, *Lecture Experiments in Chemistry*, Bell, London, 1948.
6. *International Critical Tables, Vol. V*, Mc-Graw Hill, New York, 1929, pp. 98–105.
7. *Gmelins Handbuch der anorganischen Chemie*, System No. 15, Teil B, Verlag Chemie, Weinheim, 1959, p. 675.
8. *Gmelins Handbuch der anorganischen Chemie*, System No. 35, Teil B, Verlag Chemie, Weinheim, 1933, p. 189.
9. H. Ginsberg, *Leichtmetallanalyse*, Walter De Gruyter, Berlin, 1955, pp. 121–123.
10. G. H. Osborn and W. Stross (eds.), The Association of Light Alloy Refiners, *"Modern Methods for the Analysis of Aluminium Alloys"* Chapman and Hall, London, 1949, pp. 19–21.

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