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Gas-Chromatographic Separation of Inorganic Chlorides and Its Application to Metal Analysis. II. Determination of Silicon in Iron and Steel

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Summary

The determination of silicon in iron and steel has been studied as an example of the application of gas chromatography to the analysis of metals and alloys. The method examined comprises the conversion of silicon into the volatile chloride, which is subsequently analyzed by gas chromatography.

The reaction of gaseous chlorine with iron and steel samples of different composition proved to be fast and complete under suitable conditions. When carried out on the milligram scale, the chlorination procedure can be integrated with the gas-chromatographic analysis proper. Silicon tetrachloride was formed from silicon present in iron and steel in stoichiometric amounts.

The integrated method was tested on various standard iron and steel samples, including stainless steels, and yielded satisfactory results. The repeatability is of the order of 1–2% relative (at a level of about 1 wt. % Si in the sample). The lowest detectable concentration of silicon is less than 50 ppm by weight (for a 50-mg sample).

Features of the gas-chromatographic technique include a short time of analysis (about 15 min), simplicity of operation, and adaptability to automation.

INTRODUCTION

Our previous study has shown that the gas-chromatographic separation of inorganic chlorides boiling up to about 250°C provides a means of accurate quantitative analysis of such chlorides in liquid mixtures (*1*). These results encouraged us to explore the possibility of applying the gas-chromatographic technique to some problems connected with metal analysis.

The attractive features of gas-chromatographic techniques, such as speed, sensitivity, simplicity in operation, possibility of automation, etc., appear to fullest advantage if the wet chemical route of analysis can be avoided altogether. Accordingly, we studied the possibility of the direct conversion of metals into the corresponding chlorides by means of gaseous chlorine at elevated temperatures as a step prior to the gas-chromatographic analysis proper.

The present article deals with the determination of silicon in iron and steel. This example was chosen since we believe it to be of importance in the metallurgical field and since, moreover, the known wet chemical methods are laborious and time consuming. Other examples of gas chromatography applied to metal analysis, concerning the determination of elements in nonferrous alloys, will be reported separately.

After we had concluded the experimental part of these studies, Juvet and Fisher reported on a similar method for the analysis of certain alloys, carbides, and oxides (*8*,*9*). Using elemental fluorine for the preparation of fluorides, they succeeded in determining tungsten, molybdenum, and rhenium gas chromatographically. The alloys mentioned in their paper (*9*) (molybdenum–tungsten alloys containing 30 wt. % W and a tungsten–rhenium alloy containing 96 wt. % W) are not very common ones, however. Although it is claimed (*8*) that working with elemental fluorine is not very difficult, the limited availability of this gas and the unfamiliarity of most analytical chemists with its handling should, in our opinion, render the use of chlorine more attractive. As we will show, the reactivity of chlorine is quite sufficient to allow a rapid conversion of most alloys. This even applies to some materials of construction employed by Juvet and Fisher (e.g., stainless steel and nickel), which they reported to be free from visible attack by elemental fluorine.

EXPERIMENTAL

Outline of Method

A weighed sample (1–50 mg) contained in a sample boat is introduced into a quartz tube. Next, the sample is heated at 600–900°C and gaseous chlorine passed over it. The volatile chlorides formed are collected in a trapping column while the greater part of excess chlorine is vented.

The trapping column is then switched into the gas-chromatographic circuit. With the aid of some heating, the volatile chlorides are desorbed from the trapping column and swept into the gas-chromatographic column, where they are separated. The concentration of eluted chlorides in the effluent gas is monitored by the gas-density detector.

Apparatus

Flow Diagram. Figure 1 shows the flow system with the position of the cocks corresponding with the situation at the beginning of an analysis. In the following description, figures between parentheses refer to item numbers in Fig. 1.

Nitrogen (containing some argon and less than 10 ppm oxygen as main impurities) is used as the carrier gas. Its pressure is regulated by a precision reducing valve (1) and measured by means of a precision manometer (2). Moisture, if present, is removed by a large-capacity molecular-sieves drier (3) and a smaller drier with phosphorus pentoxide (4). The dry nitrogen stream is split into three flows, each of which is controlled by a capillary restriction (5, 6, and 8). The reference flow passing through capillary (8) can be stopped by means of a valve (7) to allow the carrier gas flow through the column to be measured separately in the combined exit of the detector.

In the situation shown in Fig. 1, carrier gas passes via capillary (6) and four-way cock B to the gas-chromatographic column (13) and the detector (14). The last two are accommodated in an air thermostat (16). The combined exit stream from the detector passes via a needle valve (15) and an absorption tower (17) to the soap-film flow meter (18). The absorption tower is filled with moist KOH pellets.

The third nitrogen stream passing through capillary (5) is led via cock A to the oven tube (11) and trapping column (12) and is vented via cock B.

Chlorine gas from a lecture bottle passes through a Monel valve (9) and a phosphorus pentoxide drier (10) to four-way cock A, from where it is vented into a ventilated hood.

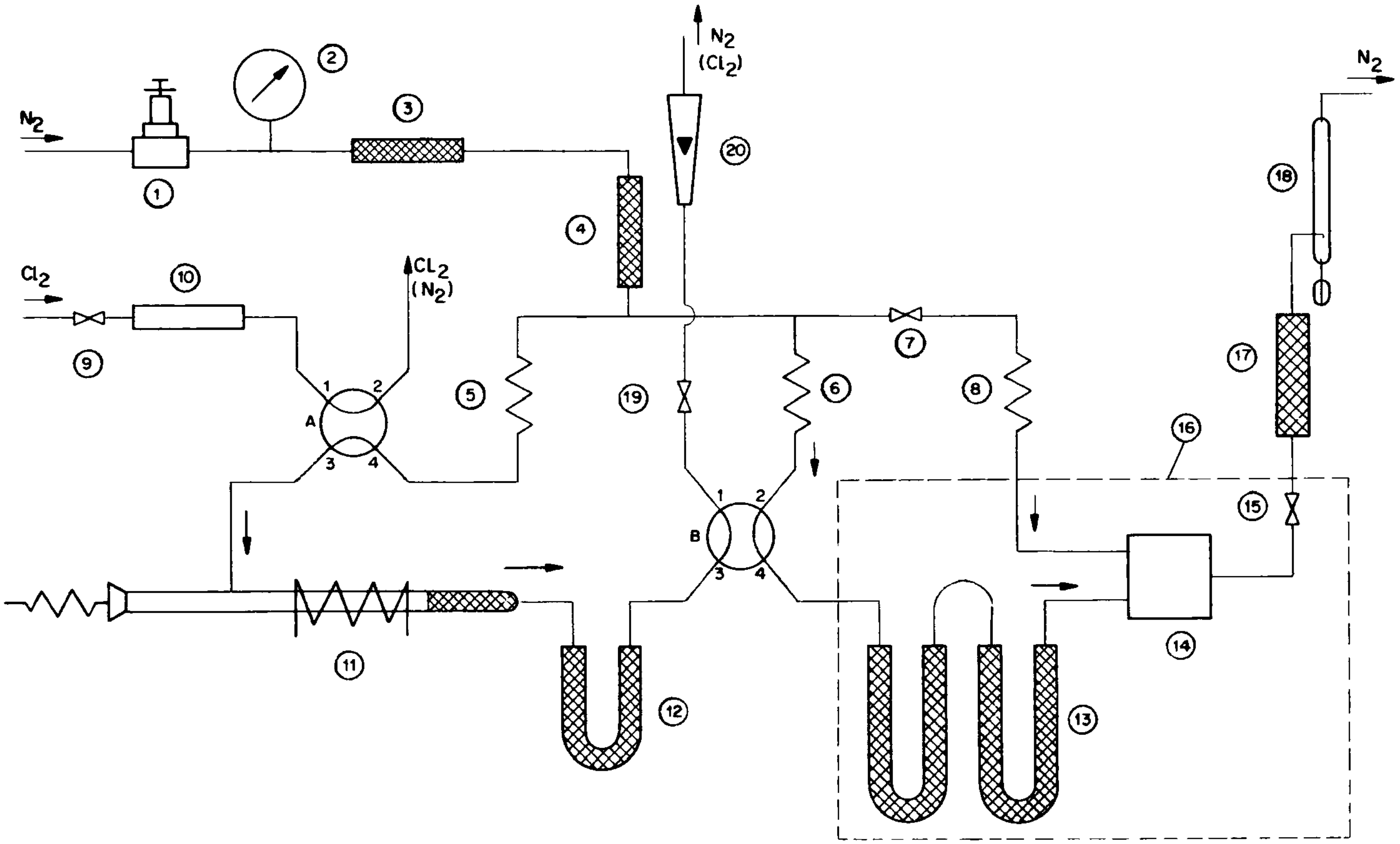

FIG. 1. Flow scheme of apparatus; numbers are explained in the text.

In the chlorination step, cock A is turned through 90°. The chlorine stream now passes through the chlorination tube and sweeps the volatile chlorides formed into the trapping column. The exit stream of this column is vented via valve (19) and rotameter (20), the latter indicating the chlorine flow rate.

Following the chlorination period, cock A is turned back to the position shown in Fig. 1. The chlorination tube is now purged with nitrogen gas.

In the subsequent chromatographic analysis, cock B is turned through 90°. Volatile chlorides collected in the trapping column are carried by a nitrogen stream through the chromatographic column.

Chlorination Tube. The chlorination tube shown in Fig. 2. is made of quartz tubing of about 1 cm i.d. The chlorination section proper can be heated electrically up to about 1000°C. The use of bare nichrome ribbon for this purpose assures rapid heating or cooling and allows visual inspection of the sample during chlorination.

The sample inlet side of the chlorination tube is closed with a stopper. This stopper is provided with a capillary leak for reasons to be disclosed below. Samples are contained in a small boat (made from quartz, graphite, or sintered alumina) which can be hooked to a quartz rod provided with a sealed-in iron core.

With the gas inlet to the chlorination tube situated as shown in Fig. 2, the emergent flow of dry nitrogen prevents ambient moisture and oxygen from entering the chlorination section when the stopper is opened. Moreover, any air trapped in the tube after closing the stopper is prevented from reaching the chlorination section by the small steady flow of gas escaping through the bleed

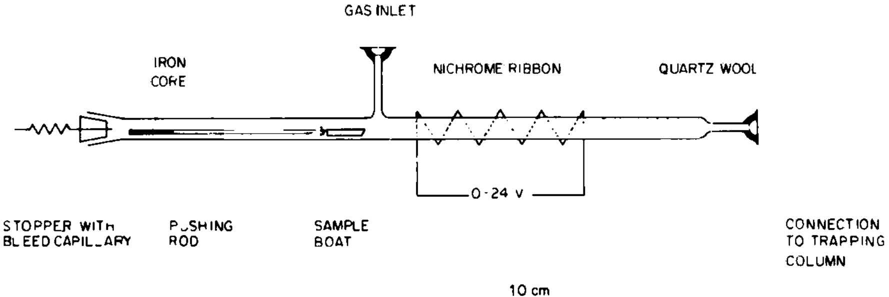

FIG. 2. Chlorination tube.

capillary. This capillary leak also has another function: Without it the sample inlet part of the chlorination tube would act as a dead pocket where some chlorine may accumulate during the chlorination period. In the analysis period, chlorine may diffuse back into the nitrogen stream, causing an undesirable tailing of the residual chlorine peak in the chromatogram.

The exit end of the quartz tube is loosely filled with quartz wool. Since this part is colder, heavier chlorides (particularly Fe_2Cl_6) are deposited here. Thus, clogging of connecting tubing by these chlorides is avoided. The solid deposits in the chlorination tube are removed from time to time.

Columns. The trapping column is a U-shaped glass tube of 8 mm i.d. and about 30 cm length. The analysis column is a W-shaped glass tube of 8 mm i.d. and 200 cm total length. The filling of both columns consists of Haloport-F* (30/80 mesh) coated with 15 wt. % of Kel-F polymer wax.†

The trapping column is normally surrounded by a Dewar flask filled with an ice-water mixture. During desorption, this flask is replaced by a hot-water bath.

The analysis column is kept in an air thermostat at 75°C (accuracy ± 0.5°C). Since the retention time of silicon tetrachloride on Kel-F columns is appreciably longer than that of BCl_3 and considerably shorter than the retention times of other metal chlorides [cf. our earlier work (*1*)], the analysis is not interfered with by other elements normally present in iron or steel.

Detector. We used a gas-density balance (Model 091 of Gow-Mac Instrument Co., Madison, N.J.) constructed of Monel. The sensing elements were Teflon-coated tungsten filaments (Gow-Mac type 9225) connected in a Wheatstone bridge arrangement with two 100-Ω resistors. Bridge current was 150 mA. The signal was registered by a potentiometric recorder (5 mV full scale).

Procedure

A sample of metal (containing preferably between 0.05 and 0.2 mg of silicon) is weighed out into a sample boat with the aid of a balance accurate to about 0.01 mg. While the cocks in the flow system have the positions shown in Fig. 1, the chlorination tube is

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* F & M Scientific Co., Avondale, Pa.

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

opened and the boat inserted into the opening of the tube. The boat is hooked to the quartz rod and pushed further inside just in front of the heated section, whereupon the tube is closed.

Cock A (see Fig. 1) is turned to allow chlorine to enter the chlorination tube and simultaneously the boat is pushed into the hot section (by means of a magnet on the outside). After a few minutes cock A is turned back to the former position, thus purging the chlorination tube and trapping column with nitrogen.

About 1 min later, cock B (see Fig. 1) is turned to connect the trapping column with the analysis column. The cold bath surrounding the trapping column is replaced by a hot-water bath, and the gas-chromatographic analysis is allowed to proceed.

After cock B has been turned back to the former position, and after cooling of the trapping column and withdrawal of the sample boat used, the apparatus is ready to accept the next sample.

RESULTS AND DISCUSSION

Factors Affecting Metal Conversion and the Recovery of Silicon Tetrachloride

Effect of Chlorination Temperature and Time on the Conversion of Metal. To determine the feasibility of a small-scale chlorination procedure which can be integrated with the chromatographic analysis, we carried out a few experiments in which a quartz boat containing 15 mg of cast iron filings was introduced into the hot oven section while the chlorine flow was started simultaneously. After a predetermined time (counted from the moment of sample introduction), the chlorine flow was stopped and replaced by nitrogen. The quartz boat was removed and the amount of unconverted metal determined by weighing.

The results, which are presented in graph form in Fig. 3, show that at 600°C a virtually complete conversion takes only 1½ min.* This means that the chlorination step can indeed be integrated with the chromatographic analysis proper.

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* The temperatures mentioned are temperatures of the oven tube. Neither true reaction temperatures nor exact reaction time can be stated. The times reported include the heating-up time of the boat and its contents. At some point in this heating-up stage, appreciable attack of the metal by chlorine starts. Since the reaction is highly exothermic, the metal particles attain temperatures even higher than the oven temperature: The metal burns away in the chlorine atmosphere.

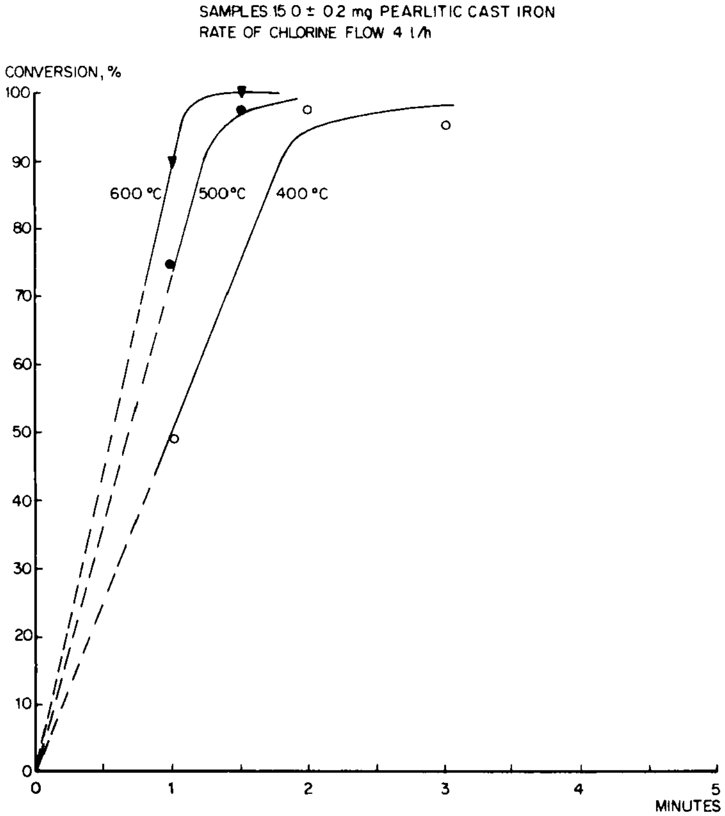

FIG. 3. Effect of oven temperature and chlorination time on conversion.

Effect of Chlorine Flow and Chlorination Time on the Recovery of Silicon Tetrachloride. In a few qualitative tests it was ascertained that the chlorination of silicon-containing iron and steel samples produced silicon tetrachloride. In runs with more emphasis on quantitative aspects, a low-alloy steel containing 0.6 wt. % Si was chlorinated at 650°C with chlorine flows of 1 and 4 liters/hr of varying duration. The relatively large samples (30 mg) consisted of drilling chips.

Excess chlorine together with volatile reaction products passed through the trapping column (kept at 0°C) with the exit open to the atmosphere. The amount of $SiCl_4$ collected in this column was subsequently desorbed and determined chromatographically.

As Fig. 4 shows, the silicon tetrachloride peak is of a constant size if the chlorination time is kept between 1½ and 3½ min at a chlorine rate of 4 liters/hr. At a shorter time a smaller peak is obtained, owing to incomplete conversion of metal (cf. previous section). In these cases a second chlorination of the unconverted residue yields the missing amount of silicon tetrachloride. If the chlorine flow is maintained over longer periods of time, some

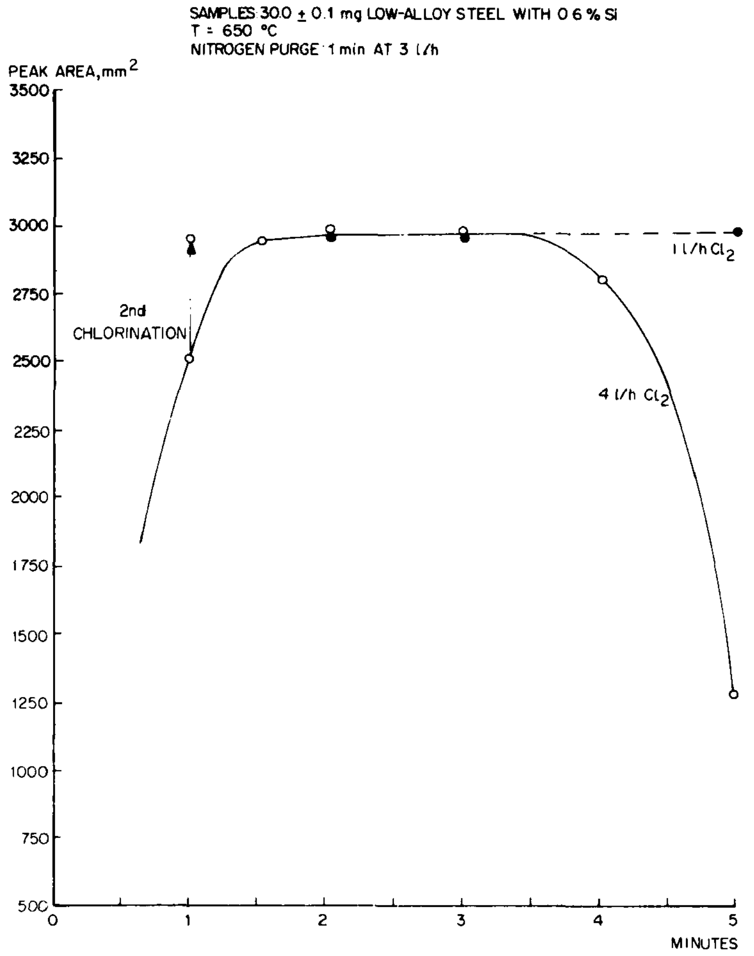

FIG. 4. Effect of chlorination time on conversion of metal and recovery of $SiCl_4$.

silicon tetrachloride is lost, owing to breakthrough of the absorption front in the trapping column.

The chlorination time can be made less critical by adopting a smaller chlorine flow, viz., 1 liter/hr. As follows from Fig. 4, conversion at this rate of flow is complete after 2 min and no silicon tetrachloride is yet lost at 5 min.

Effect of Purging with Nitrogen. Since the internal volume of the chlorination tube and the trapping column is fairly large, the system contains an appreciable excess of chlorine vapor after completion of the chlorination step. If this amount of chlorine were passed

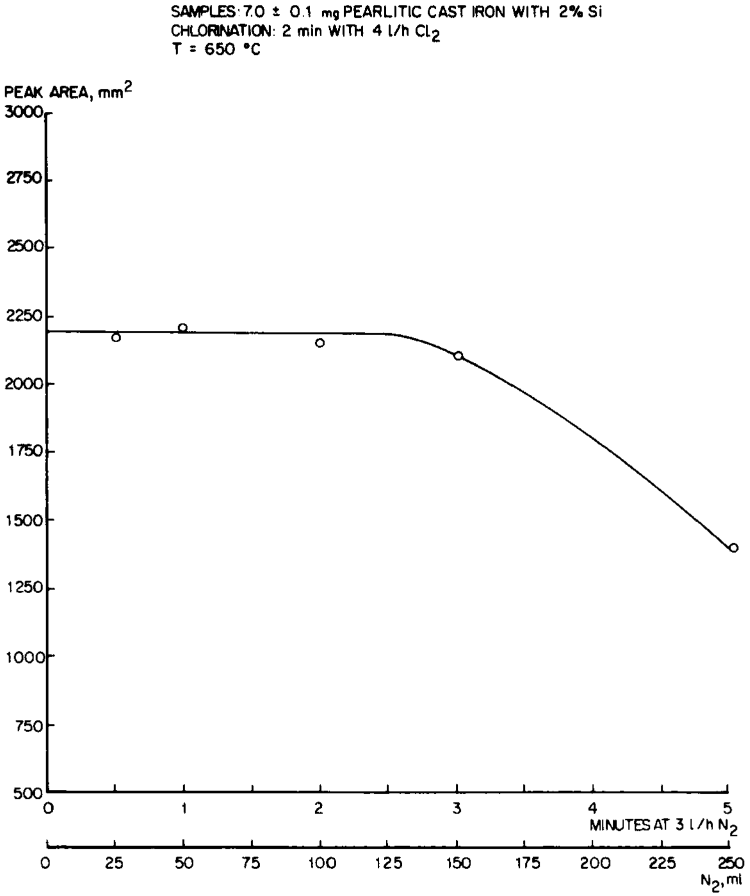
SAMPLES: 7.0 ± 0.1 mg PEARLITIC CAST IRON WITH 2% Si
CHLORINATION: 2 min WITH 4 l/h Cl_2
T = 650 °C

FIG. 5. Effect of nitrogen purge on recovery.

through the detector, the accuracy of the analysis would be adversely affected because the silicon tetrachloride peak must be measured on the tail of a very large chlorine peak. We therefore preferred to remove the larger part of chlorine by a nitrogen purge prior to the gas-chromatographic analysis. With the setup according to Fig. 1, this is very easily done.

Figure 5 shows that no silicon tetrachloride is yet lost (by breakthrough of the absorption front) if the purging period is kept shorter than 2½ min at a nitrogen flow of 3 liters/hr. A purging period of 1 min proved adequate for removing excess chlorine to such an extent that interference from the residual chlorine peak is virtually eliminated.

Stoichiometry of Silicon Tetrachloride Formation

Linearity of Response. Samples of iron and steel weighed to the nearest 0.01 mg were analyzed under the following standard conditions:

Oven temperature: 650°C
Chlorination: 2–4 min with 1.5–2 liters/hr of chlorine
Stripping: 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)

Examples of chromatograms obtained are shown in Figs. 6 and 7.

From the results presented in Figs. 8 and 9, it can be seen that the linearity of response is very satisfactory for samples of both high and low silicon content.

Blank Value. Since the straight lines in Figs. 8 and 9 all pass through the origin, the blank value must be low. This was confirmed by analyzing samples of spectroscopically pure iron. No silicon tetrachloride peaks were observed in the chromatograms. Evidently, there is no significant formation of silicon tetrachloride by reaction of quartz with chlorine under the prevailing conditions.

Calibration with Liquid Samples Containing Silicon Tetrachloride. To check whether silicon present in the metal samples is quantita-

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* Kept constant during each series of measurements.

tively converted into the tetrachloride, we compared the size of the silicon tetrachloride peaks obtained by analysis of cast iron samples of known silicon content with those from liquid calibration mixtures of known silicon tetrachloride content. Samples of the latter (5–10 μl) were injected with a microsyringe via a provisional injection port. It turned out that the yield of the tetrachloride from silicon present in the metal is 97 ± 5%. The actual yield may well have been even closer to 100%, but the limited ac-

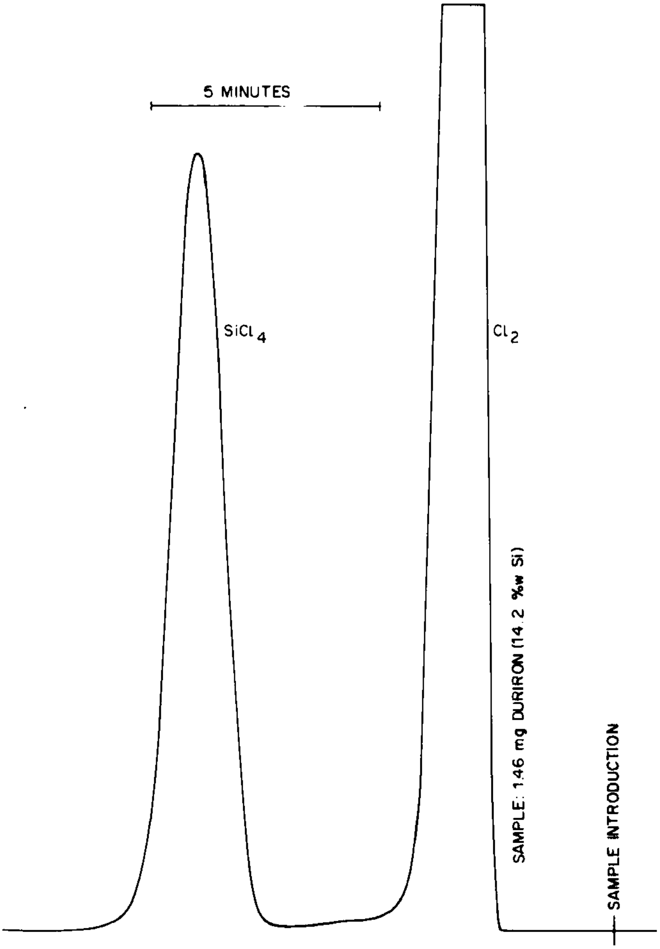

FIG. 6. Analysis of an iron sample of high silicon content.

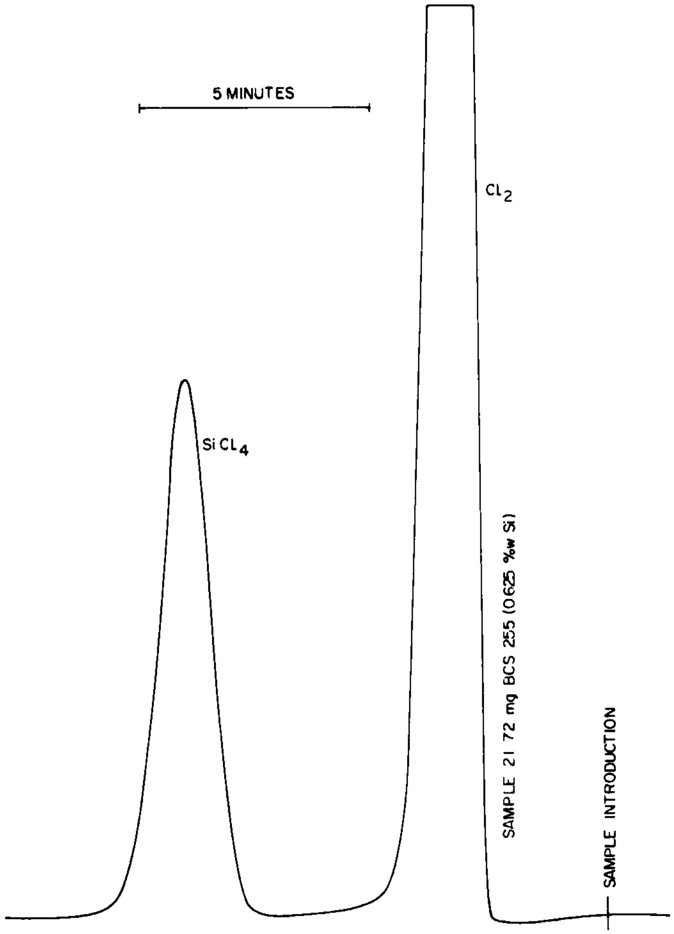

FIG. 7. Analysis of a steel sample.

curacy of injection of liquid samples does not permit a more definite conclusion.

Precision of the Method

Analysis of Standard Iron and Steel Samples. A number of iron and steel samples of known silicon content were analyzed under the conditions specified in the section on linear response. They included National Bureau of Standards (NBS) and British Chemical

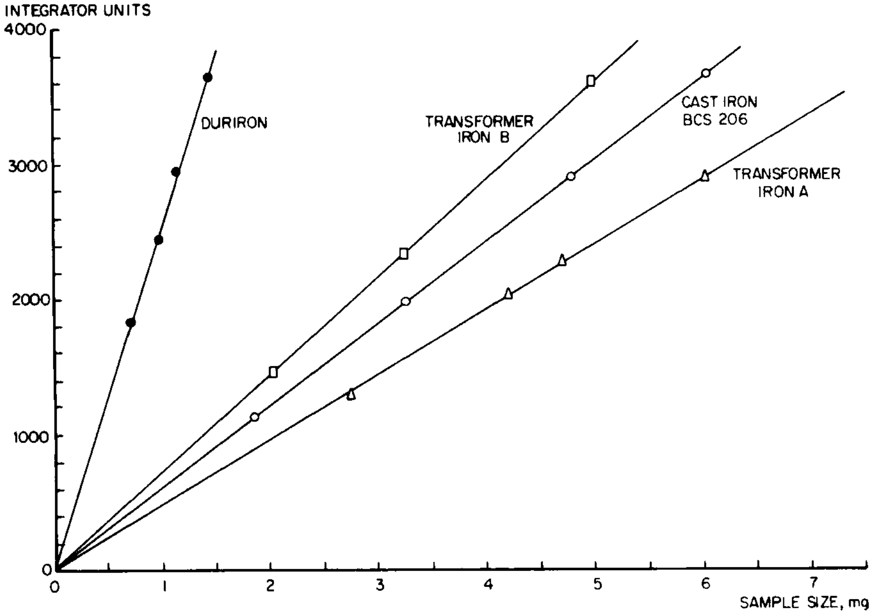

FIG. 8. Linearity of response for iron samples of high silicon content.

Standards (BCS) samples, as well as other products of which the silicon content had been determined before by a gravimetric method. The samples were examined in various forms, ranging from fine filings (particle size about 0.05 mm) to chips obtained by drilling or turning.

Since calibration with liquids is less accurate than the metal analysis appears to be, we selected one standard steel sample (BCS 255 with 0.625 wt. % Si*) to calibrate the apparatus. Calibration was performed occasionally, usually before and after a series of analyses carried out in the course of 1 day.

Table 1 presents the results obtained for different iron samples and Table 2 those obtained for samples of carbon as well as alloy steels. Chlorination of the latter steels (including the common types of stainless steel) proved to be no more difficult than that of ordinary iron and steel. It is readily seen from Tables 1 and 2 that the values obtained by the present method are in good agreement with the true values.

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* Mean of results reported by 12 different laboratories. These results show a maximum deviation from the mean of 2.4% relative and a standard deviation of 1.2% relative.

Repeatability. Table 3 presents some results of repeated analyses of the steel sample used as calibration standard. The analyses were carried out on different days in the course of 2 weeks. The results show a standard deviation from the mean of about 1.2% relative.

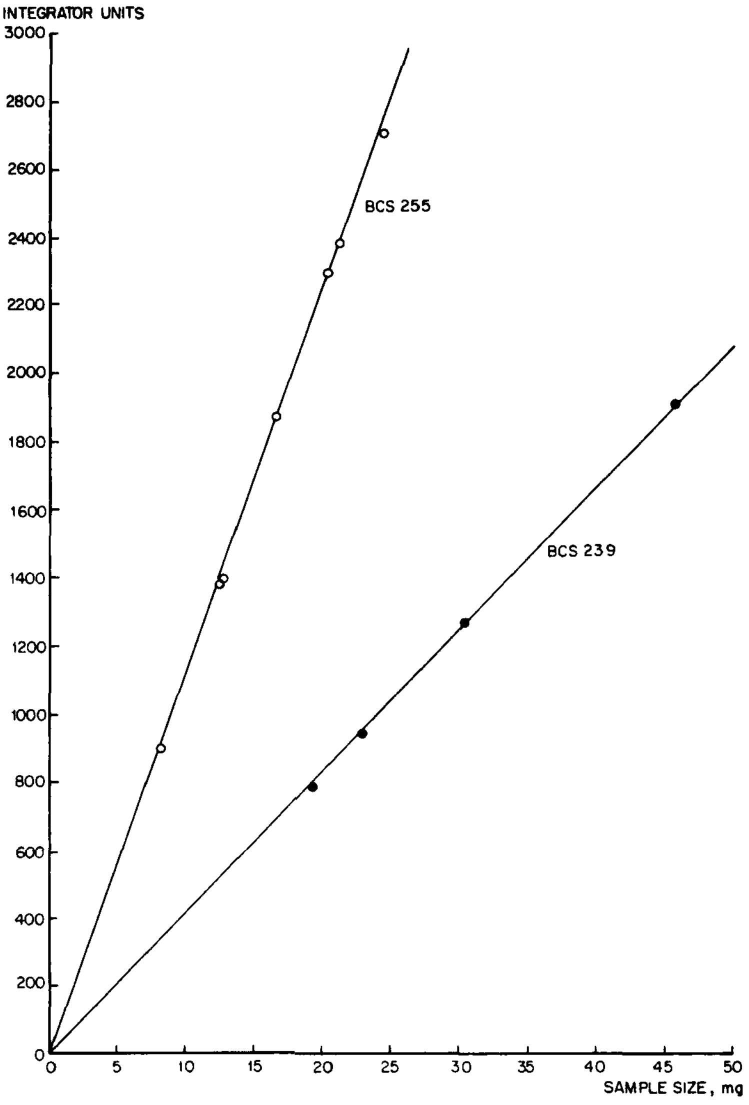

FIG. 9. Linearity of response for alloy steels of low silicon content.

TABLE 1

Analysis of Iron Samples

Sample	Composition, wt. %[a]	Wt. range, mg	No. of determinations	Si, wt. %		Max. dev. from mean, wt. %	Dev. from known value, wt. %
				Known value	Mean found		
Cast iron, BCS D2 170	1.6 Mn, 1.1 P	3.0–14	4	1.31	1.30	0.03	−0.01
Cast iron, BCS 206	2.6 C, 1.5 P, 0.3 Mn, 0.2 Ti, 0.1 V	1.8–6.0	4	3.32	3.30	0.02	−0.02
Cast iron, Pearlitic	2.8 C, 0.6 Mn, 0.2 P	2.0–10	2	2.15	2.09	0.03	−0.06
Transformer iron (A)	—	2.7–6.1	4	2.8	2.73	0.03	−0.07
Transformer iron (B)	—	2.0–5.0	3	4.2	4.10	0.01	−0.1
Duriron	0.9 C	0.7–1.5	4	14.2	14.3	0.2	+0.1

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

TABLE 2

Analysis of Steel Samples

Sample	Composition, wt. %[a]	Wt. range, mg	No. of determinations	Si, wt. %		Max. dev. from mean, wt. %	Dev. from known value, wt. %
				Known value	Mean found		
Carbon steel, BCS 215	0.9 C, 0.4 Mn, 0.1 Ni	19–50	4	0.26	0.280	0.005	+0.02
Carbon steel, BCS 239	0.7 Mn, 0.3 C, 0.3 Cu, 0.2 Ni, 0.1 Cr	19–50	4	0.24	0.230	0.004	−0.01
Low-alloy steel, BCS 254	2.1 Ni, 1.3 Mo, 0.5 Mn, 0.5 Cr, 0.5 V	15–40	5	0.295	0.298	0.006	+0.003
Low-alloy steel, BCS 257	1.7 Cr, 1.4 Mn, 0.8 Ni, 0.3 Mo, 0.3 Cu, 0.1 V	13–39	5	0.375	0.383	0.007	+0.008
Low-alloy steel, BCS 256	2.3 Cr, 1.2 Mn, 0.5 Mo, 0.4 V, 0.2 Cu, 0.2 Ni	41–50	2	0.130	0.129	0.001	−0.001
Low-alloy steel, BCS 253	2.9 Ni, 1.0 Mo, 0.5 Cu, 0.4 Mn, 0.4 Cr, 0.2 V	39–46	2	0.180	0.180	0.001	0.000
Nickel steel, BCS 252	4.1 Ni, 0.5 V, 0.2 Cr, 0.1 Cu	22–50	2	0.245	0.244	0.001	−0.001
Nickel steel, BCS 251	5.2 Ni, 0.2 Mo, 0.2 Mn	48–50	4	0.013	0.010	0.002	−0.003
Stainless steel, BCS 235	19.0 Cr, 8.7 Ni, 1.0 Cu, 0.7 W, 0.6 Ti, 0.5 Mn, 0.1 C	13–20	2	0.82	0.790	0.000	−0.03
Stainless steel, NBS 160	19.1 Cr, 8.9 Ni, 3.0 Mo, 0.7 Mn	9–15	3	1.13	1.11	0.02	−0.02
Stainless steel, NBS 123a	18 Cr, 11 Ni, 0.8 Nb, 0.1 Mo, 0.1 W	18–22	4	0.46	0.440	0.018	−0.02

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

TABLE 3

Repeatability of Gas-Chromatographic Method[a]

Determination no.	Integrator units/mg	
	Series I	Series II
1	111.5	131.8
2	112.2	130.5
3	113.9	129.0
4	113.9	133.0
5	116.0	130.2
6	114.6	129.4
7	114.9	131.5
8	114.4	131.7
9	112.5	134.4
10	111.7	132.1
11	112.3	132.1
12	111.0	130.5
Mean of 12 determinations	113.2	131.4
Max. dev. from mean, %	2.5	2.3
Standard dev., %	1.3	1.1

[a] Samples: 10–25 mg steel (BCS 255, 0.625 wt. % Si). Series I and II were conducted at somewhat different flow settings. Determinations of both series were carried out on different days in periods of 2 weeks.

Hence, the present method is roughly of the same accuracy as the usual wet chemical methods for the determination of silicon in iron and steel.

Lowest Detection Limit. If the largest sample that can be handled is taken to be 50 mg, the detection limit is conservatively estimated at 50 ppm of silicon in metal.

Sampling Errors. Since the sample size in the present method is about one-hundredth of that in standard gravimetric methods [e.g., ASTM E 30–56, Ref. (2)], the problem of representative sampling may be aggravated. The question arises whether sample inhomogeneity is such as to interfere with the accurate determination of silicon in iron and steel on the scale proposed here.

In the analysis of different iron and steel samples, however, we observed no effects that can be traced back to appreciable sample inhomogeneity. The satisfactory results obtained (see Tables 1–3) prove that small-scale analysis of iron and steel is possible. They also indicate that the problem of representative sampling is not a very serious one, at least not for the determination of silicon in the usual iron and steel samples.

In support of this conclusion we conducted some statistical calculations to assess the effect of various degrees of sample heterogeneity on the accuracy of the analysis. From these considerations it turned out that the sampling error is only likely to be very serious in a case where pure or almost pure silicon is admixed with a large proportion of silicon-free iron. Actual experiments with such a physical mixture indeed gave an appreciable spread in the analytical results.

Still, we do not believe that a case like the above one is representative of actual practice. As may be deduced from the temperature–composition diagram of the Fe–Si binary system [see, e.g., Ref. (3)], silicon can remain in solid solution in iron up to percentages far above those encountered in ordinary iron and steel. This is in contrast to carbon, which has an extremely low solubility in iron and easily separates out as graphite or cementite (Fe_3C).

In consequence, the sampling problem caused by small-scale segregation appears to be far less serious in a silicon analysis than in a determination of carbon in iron or steel.

In the casting of iron or steel objects, the transition from the liquid to the solid state may lead to segregation of elements, with concentration differences extending over relatively great distances. A sample taken from such an object by drilling at several locations may, therefore, consist of chips of different compositions. However, from the temperature–composition diagram of the Fe–Si system, it can again be deduced that this type of macrosegregation is not likely to be very serious. An experimental study of the segregation of elements in steel ingots [by the Heterogeneity of Steel Ingots Committee (4)] showed that the distribution of silicon is fairly uniform, in contrast to the distinct segregation observed with carbon, sulfur, and phosphorus.

Summarizing, the segregation of silicon in iron and steel does not appear to be a matter of great moment. This view is also taken by several authors of monographs on iron and steel (5–7).

CONCLUDING REMARKS

The present study demonstrates that silicon in iron and steel can be determined by gas chromatography via the chloride route. As regards accuracy, the gas-chromatographic technique compares favorably with the usual methods of silicon determination.

The very small samples required will in some instances be advantageous, e.g., when small objects must be examined or when the object of study is distinctly heterogeneous. In the latter case it may be possible to examine different parts of the object separately, e.g., a superficial layer and the interior.

The gas-chromatographic method is considerably faster than the usual gravimetric methods for silicon determination; an analysis normally takes only about 15 min. Another distinct advantage is its simplicity. Whereas the wet chemical methods involve a good deal of handling, a gas-chromatographic analysis (with the apparatus properly set up and calibrated) requires only a few manipulations, viz., weighing of the sample, introducing it into the oven tube, occasional turning of a cock, and a temporary heating of the trapping column.

Most of the above steps can be automated for additional saving of labor in serial analyses. On the basis of the present integrated method of chlorination and gas-chromatographic analysis of silicon tetrachloride, it should be possible to devise an apparatus that accepts a series of weighed samples to be analyzed successively in unattended operation. Furthermore, methods analogous to the present one may, in principle, be worked out for the determination of other elements in iron and steel, e.g., for titanium, tin, and arsenic.

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