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**A COMPARISON OF THE CHEMICAL ANALYSIS OF  
SILICON IN FERROSILICON USING A GRAVIMETRIC  
OR A SINGLE COLUMN ION CHROMATOGRAPHIC METHODOLOGY**

**Steven Allen Kirby**

**A Thesis  
in  
The Department  
of  
Chemistry and Biochemistry**

**Presented in Partial Fulfillment of the Requirements  
for the Degree of Master of Science at  
Concordia University  
Montreal, Quebec, Canada**

**August 1989**

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## ABSTRACT

A COMPARISON OF THE CHEMICAL ANALYSIS OF  
SILICON IN FERROSILICON USING A  
GRAVIMETRIC OR SINGLE COLUMN ION  
CHROMATOGRAPHIC METHODOLOGY

Steven Allen Kirby

This study provided an objective comparison of two methodologies for the analysis of silicon in ferrosilicon samples. The accepted methodology involved the fusion of the ferrosilicon sample with a sodium hydroxide flux, followed by a dehydration step using acid and finally a gravimetric determination of the amount of silicon present as silicon dioxide. The other methodology again involved a fusion of the ferrosilicon sample, however, the analysis was performed using SCIC (Single Column Ion Chromatography) employing a sodium hydroxide eluent.

The basic criteria for the replacement of the gravimetric methodology with the SCIC methodology were: (1) the SCIC methodology developed must be faster, on an industrial scale, than the gravimetric methodology; (2) the SCIC methodology must be capable of providing results having at least equivalent or better reproducibility than its gravimetric counterpart. The results, obtained by this author indicate that the SCIC methodology developed, including the required pretreatment of the samples, could not meet either of these requirements. First, the time saved

using the SCIC methodology was relatively insignificant. Second, the SCIC methodology could not provide the same level of reproducibility since the small change in conductance signal ( $\Delta G$ ), observed as the silicate peak, was read upon a high background conductance (from the sodium hydroxide eluent) observed as the baseline. Hence, this method provided a poor signal to noise ratio, which is undesirable for any analytical methodology.

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Finally, I would like to dedicate this thesis to Anyck, my parents and the rest of our families for their encouragement and understanding during this work.

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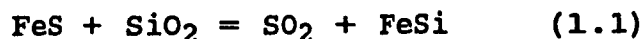
## **1 THE ANALYSIS OF SILICON IN FERROSILICON**

### **USING A GRAVIMETRIC METHODOLOGY**

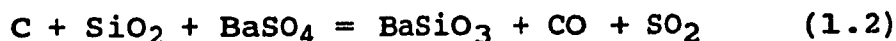
#### **1.1 INTRODUCTION TO THE GRAVIMETRIC METHODOLOGY**

The alloys of silicon-iron or iron silicides are made commercially to be used in the production of steel. There have been a large number of these silicides reported. In fact, silicides having an iron to silicon ratio of 3:1, 2:1, 5:2, 3:2, 1:1, 3:4, 1:3 and 1:2 have been reported<sup>1</sup>. The silicides are used as both deoxidizers and to introduce a specified amount of silicon to the steel itself. Formerly the silicides were produced in blast furnaces ( i.e. 1250-1800 °C) and they contained between 14 percent to 20 percent silicon <sup>1,2</sup>. However, today the silicides are made in electric furnaces with silicon contents of 15 to 90 percent. The term "ferrosilicon" has been recommended by Donath and Haissig<sup>2</sup> to represent iron silicides having silicon contents of greater than 5 percent. Ferrosilicon is commercially made in many grades depending on the content of the silicon. The different grades of ferrosilicon commercially available are listed by ASTM<sup>3</sup> as well as their respective specifications. These values were adapted from the literature source and they are shown in Tables 1.1 and 1.2.

A large number of patents have been registered for the preparation of ferrosilicon. A mixture of quartz and iron sulphide was used by Aschermann<sup>4,5</sup> to prepare ferrosilicon:



Gin<sup>6</sup> used a mixture of quartz, ferric oxide, carbon and barium sulphate in the synthesis of ferrosilicon. The reactions have been represented by the author as follows:



The accepted technique for the analysis of silicon in ferrosilicon involves the decomposition of the ferrosilicon to silicates by fusion with sodium peroxide as the fusion flux<sup>7,8,9,10,11</sup>. In fact fusion with mixtures of sodium peroxide and sodium carbonate have also been used<sup>8,11</sup>. Once the decomposition is complete a gravimetric methodology is used to separate and quantify the silicon as silicic acid<sup>8,11</sup>.

The following brief point by point description of the operations involved in the gravimetric determination of silicon in silicates was given by Egorova<sup>8</sup>. These steps are also used in the specific analysis of silicon in ferrosilicon once the decomposition of the ferrosilicon has been achieved. The steps are as follows: (1) the

finely-divided iron silicide (note that ferrosilicon is difficult to grind) is fused forming sodium silicates and the cooled melt is then decomposed with the addition of acid, forming silicic acid; (2) the acid solution is evaporated to dryness, to ensure that the dehydration of the silicic acid is complete and that it is converted to the insoluble state; (3) water is added to dissolve the soluble salts; (4) the silicic acid is filtered and washed; (5) the filtrate is re-evaporated to precipitate any residual silicic acid remaining in the filtrate and this is then followed by the repetition of steps (3) and (4); (6) both precipitates of silicic acid are ignited together to constant weight as silicon dioxide; (7) a controlled treatment of the dehydrated silicon dioxide product by a mixture of HF and H<sub>2</sub>SO<sub>4</sub> is finally performed to volatilize the silicon as silicon tetrafluoride. The HF reacts with the silicon dioxide forming the volatile compound silicon tetrafluoride (SiF<sub>4</sub>) and water :



The determination of the amount of silicon present is achieved by finding the difference in the weight before and after the HF treatment (i.e. by the loss in weight).



## **1.2 EXPERIMENTAL SECTION**

### **1.2.1 MATERIALS AND REAGENTS**

The NBS and unknown ferrosilicon samples were obtained from the Science Industrial Research Unit (S.I.R.U.) at Concordia University. The certificate of analysis for the NBS standard was not available from the National Institute of Standards and Technology (NIST) of the U.S. Department of Commerce, however, it was listed as 75% silicon. All the other chemicals (HCl, HClO<sub>4</sub>, HF, NaOH, Na<sub>2</sub>O<sub>2</sub> and KOH) used during the gravimetric methodology were reagent grade.

### **1.2.2 GRAVIMETRIC EXPERIMENTAL PROCEDURE**

The samples of ferrosilicon (.35 g) were weighed into 30 ml nickel crucibles. A 10:1 ratio (i.e 3.5 g) of reagent grade sodium hydroxide fusion flux was added to each of the nickel crucibles (note: a blank was also carried throughout the following procedure). The crucibles were covered with a nickel crucible cover to eliminate sample losses caused by spattering during the fusion process. The crucible covers had small holes drilled through them to allow for the exit of the hydrogen gas produced during the fusion reaction. The crucibles were then placed on a hot plate to melt the flux and start the fusion reaction, hence, evolving

some of the hydrogen gas before actually fusing over an open flame. Once the flux was entirely melted each crucible was placed over a hot flame (approximately 700 °C), provided by a Bunsen burner, and the crucible was rotated vigorously, using crucible tongs, to aid in the formation of a homogeneous fusion melt. At this point caution was employed because the hydrogen gas was evolved so rapidly that the unsecured crucible covers were often blown completely off the crucibles. The crucibles were finally placed in a muffle furnace, at 900 °C, for ten minutes to ensure that the fusion was complete.

The crucibles were removed from the muffle furnace to cool. The crucible contents were quantitatively transferred, employing a glass stirring rod and rubber policeman, to a 600 ml beaker containing 20 ml of concentrated hydrochloric acid (HCl), 20 ml of concentrated perchloric acid (HClO<sub>4</sub>) and 20 ml of deionized water. The transfer of the crucible contents was aided by rinsing with hot deionized water (approximately 150-200 ml). The solutions, which contained the insoluble silicates, were placed on a hotplate and boiled carefully (to avoid "bumping") until about 50 ml of solution remained. The beakers were partially covered and the temperature of the

hotplate decreased substantially to boil off the remaining liquid and to avoid the occurrence of "bumping" of the thick "gel like" polymerized silicic acid. The contents of the beaker were then heated to "dense fumes" of perchloric acid and cooled.

Approximately 100 ml of hot deionized water was added to each beaker and the contents were quantitatively transferred, using a glass stirring rod with a rubber policeman attached, and with periodic rinsing, into a long stem glass funnel, where the insoluble polymerized silica was filtered off using Whatman #42 (ashable) filter paper. The filtrate was collected in a 400 ml beaker. The quantitative transfer and rinsing steps were repeated until all the insoluble silica had been transferred from the beaker to the filter paper. The silica remaining on the filter paper was rinsed with a total of approximately 100 ml of 5% HCl, and then with a total of about 100 ml of hot deionized water to remove any remaining perchlorate salts. The filter paper containing the silicates was placed in a platinum crucible. Each of the 400 ml beakers containing both the filtrate and combined rinsings was placed back on the hot plate and again boiled down to "fumes" of perchloric acid. The filtering step was then repeated, and the filter paper and remaining silica

collected was placed in the proper platinum crucible. The filtrate remaining after the second filtration step was then discarded.

The platinum crucibles were covered and heated over a low Bunsen burner flame to burn off the carbon present in the filter paper (i.e. "ash it"). The covered crucibles were placed in a muffle furnace (at 850 °C) for 45 minutes to complete the ashing process. The crucibles were then cooled in a desiccator. The crucibles were weighed to the nearest .1 mg using an analytical balance. This heating and cooling process was repeated until a constant weight was obtained, that is that two successive heating and weighing steps produced no more than a .2 mg change in the weight of the crucible and its contents. The weights were recorded.

Once a constant weight had been established, five drops of concentrated  $\text{H}_2\text{SO}_4$  and ten ml of HF were carefully added to each crucible, producing the volatile compound  $\text{SiF}_4$ . The crucibles were then placed on a hot plate to complete the volatilization of  $\text{SiF}_4$ . The remaining HF was boiled off until only a precipitate remained. The crucible was then heated over a flame to remove any possible remaining HF and to re-oxidize any salts (note: these steps were performed

in a fume hood to avoid the toxic and corrosive effects of the "extremely dangerous" chemical HF). The crucibles were placed in the muffle furnace again (at 850 °C) and heated for ten minutes. They were removed, cooled in a desiccator and reweighed until constant weight was obtained for each.

### 1.3 RESULTS

The amount of silicon (in percent), in the original ferrosilicon sample, was calculated from the difference in the weights before and after the HF treatment. The difference between the weights represented the loss of silicon dioxide as the volatile compound  $\text{SiF}_4$ <sup>8,11</sup>. The equation used to calculate the percent silicon in the original ferrosilicon sample was:

$$\% \text{ Si} = (A-B) \times .4672 / C \times 100 \quad (1.5)$$

where A = weight of  $\text{SiO}_2$  lost by conversion to  $\text{SiF}_4$  (g)

and B = correction for blank (g)

and C = the original sample weight of the ferrosilicon sample (g)

The value of .4672 is the gravimetric factor for the molecular weight of silicon over the molecular weight of silicon dioxide<sup>11</sup>.

The rejection criteria used, for any suspect gravimetric results, was the 3.3 s rule. If the ratio of the deviation for any suspect value divided by the standard deviation (s) was greater than 3.3 the result was rejected with a 99.9% probability that the rejection was valid. If the result was rejected an asterix (\*) is

shown, in Tables 1.3 through 1.9, to denote this. The average and standard deviation were then recalculated without the rejected value.

**TABLE 1.1**

**THE ASTM FERROSILICON CHEMICAL REQUIREMENTS, IN**  
**PERCENTAGE, FOR THE DIFFERENT STEEL MAKING GRADES**

<u>grade of</u> <u>ferro-</u> <u>silicon</u>	<u>silicon</u>	<u>carbon</u>	<u>phos-</u> <u>phorus</u>	<u>alum-</u> <u>inum</u>	<u>manganese</u>
A	92-95%	0.10%	0.025%	2.00%	0.25%
B	83-88%	0.15%	0.030%	1.75%	0.35%
C	74-79%	0.10%	0.035%	1.50%	0.40%
D	65-70%	0.10%	0.035%	1.25%	0.50%
E	47-51%	0.10%	0.040%	1.25%	0.75%
F	20-24%	0.50%	0.120%	1.00%	1.00%
G	14-17%	0.70%	0.120%	0.75%	1.25%



**TABLE 1.2**

**THE ASTM FERROSILICON CHEMICAL REQUIREMENTS, IN**  
**PERCENTAGE, FOR THE DIFFERENT FOUNDRY GRADES**

<u>grade</u>	<u>silicon</u>	<u>carbon</u>	<u>phos-</u> <u>phorus</u>	<u>aluminum</u>	<u>manganese</u>	<u>boron</u>
B1	83-88%	0.15%	0.030%	1.25-1.75%	0.35%	...
B2	83-88%	0.15%	0.030%	1.25-1.75%	0.35%	...
C1	74-79%	0.10%	0.035%	1.00-1.50%	0.40%	...
C2	74-79%	0.10%	0.035%	1.00-1.50%	0.40%	...
E1	47-51%	0.10%	0.040%	1.25% max	0.75%	.04-.1%
F1	20-24%	0.50%	0.120%	1.00% max	1.00%	.04-.1%
G1	14-17%	0.70%	0.120%	0.75% max	1.25%	.04-.1%

**TABLE 1.3****THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE SILICON**  
**IN THE NBS FERROSILICON STANDARD (75% Si)**

<b><u>run#</u></b>	<b><u>percentage (%) silicon</u></b>
1	75.07
2	75.07
3	75.11
4	75.20
5	74.90
6	75.37
7	74.90
8	75.50
9	74.94
10	75.14
11	74.66
12	75.10
13	75.12
14	75.00
15	74.95
16	75.20
17	74.98
18	75.02
19	75.16

**TABLE 1.4****THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE  
SILICON IN FERROSILICON UNKNOWN #1**

<b><u>run #</u></b>	<b><u>percentage (%) silicon</u></b>
1	48.40
2	47.88
3	47.68
4	47.51
5	47.56
6	48.30
7	47.70
8	47.69
9	47.81
10	47.93
11	48.10
12	48.47
13	48.24
14	47.89
15	47.92
16	47.80
17	48.00
18	48.10
19	48.15
20	47.19
21	47.54

**TABLE 1.5****THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE**  
**SILICON IN FERROSILICON UNKNOWN #2**

<b><u>run#</u></b>	<b><u>percentage (%) silicon</u></b>
1	29.68
2	30.54
3	30.25
4	30.10
5	30.27
6	30.14
7	30.19
8	30.41
9	30.37
10	30.34
11	29.86
12	30.24
13	30.19
14	30.14
15	30.21
16	30.23
17	30.22
18	30.31

**TABLE 1.6**

**THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE**  
**SILICON IN FERROSILICON UNKNOWN #3**

<u>run #</u>	<u>percentage (%) silicon</u>
1	47.50
2	47.90
3	47.87
4	47.67
5	47.60
6	47.57
7	47.51
8	47.73
9	48.07
10	48.03
11	47.83
12	47.78
13	47.89
14	47.60
15	47.80
16	47.85
17	47.39
18	47.90
19	47.67

**TABLE 1.7****THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE**  
**SILICON IN FERROSILICON UNKNOWN # 4**

<b><u>run #</u></b>	<b><u>percentage (%) silicon</u></b>
1	75.14
2	75.63
3	75.91
4	75.21
5	75.71
6	75.94
7	75.69
8	75.09
9	75.63
10	75.21
11	75.26
12	75.57
13	76.10
14	75.63
15	75.38
16	75.59
17	75.09
18	75.50
19	75.59
20	75.41
21	75.39

**TABLE 1.8****THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE**  
**SILICON IN FERROSILICON UNKNOWN #5**

<u>run #</u>	<u>percentage (%) silicon</u>
1	51.40
2	51.30
3	51.15
4	51.29
5	51.16
6	51.38
7	51.91
8	52.72 *
9	51.32
10	51.49
11	51.57
12	51.93
13	51.22
14	51.45
15	51.25
16	51.37
17	51.94
18	51.43
19	51.95
20	52.03
21	51.21
22	51.28
23	51.21
24	51.24
25	52.03
26	52.10

**TABLE 1.9**

**THE GRAVIMETRIC RESULTS FOR THE PERCENTAGE**  
**SILICON IN FERROSILICON UNKNOWN # 6**

<b><u>run #</u></b>	<b><u>percentage (%) silicon</u></b>
1	16.09
2	15.72
3	16.22
4	15.90
5	16.41
6	15.98
7	15.78
8	15.99
9	16.02
10	16.22
11	16.06
12	16.33
13	15.82
14	16.10
15	15.98
16	15.90
17	16.12
18	16.20
19	16.31
20	15.83
21	15.87



**TABLE 1.10**  
**THE GRAVIMETRIC RESULTS FOR THE NUMBER, AVERAGE**  
**PERCENTAGE SILICON (%Si) AND STANDARD DEVIATION**  
**FOR THE FERROSILICON SAMPLES**

<u>ferrosilicon</u> <u>sample</u>	<u>number (N)</u>	<u>average per-</u> <u>centage (%)</u> <u>silicon</u>	<u>standard</u> <u>deviation</u>
NBS	19	75.07	.18
unknown # 1	21	47.90	.32
unknown # 2	18	30.20	.19
unknown # 3	19	47.75	.19
unknown # 4	21	75.51	.29
unknown # 5	25	51.51	.36
unknown # 6	21	16.04	.19

#### **1.4 CRITIQUE OF THE GRAVIMETRIC METHODOLOGY**

The gravimetric method employed in this work, for the analysis of silicon in ferrosilicon, was a modified version of the methodology found in the ASTM designation E 360, titled "silicon by the sodium peroxide fusion method"<sup>11</sup>. Three different fusion fluxes were tried including sodium peroxide, sodium hydroxide and potassium hydroxide. The author found that the sodium hydroxide and ferrosilicon fusion reaction was less violent and easier to control (although the evolution of hydrogen gas presented a problem) than the sodium peroxide and ferrosilicon fusion reaction. In fact the violent nature of the latter fusion reaction reduced the nickel crucible's "life time" substantially, because it caused the formation of holes on the side or bottom of the crucible. When employing sodium peroxide as the fusion flux the reaction was so exothermic that the heat produced often caused the nickel crucibles to "glow" red and even white. The sodium hydroxide fusion flux was preferred to the potassium hydroxide flux because of the difficulty in removing (i.e. washing off) the potassium perchlorate salts formed during the dehydration of the silicic acid. These factors led to the choice of sodium hydroxide as the fusion flux in this work.

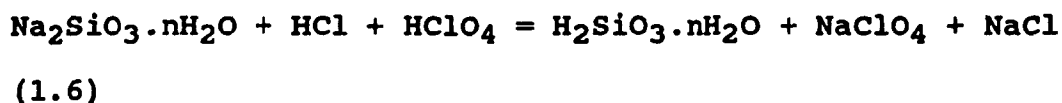
The quantitative gravimetric results, calculated as the percentage silicon, presented in Tables 1.3 through 1.9 for the NBS (National Bureau of Standards) ferrosilicon standard (certified as 75% silicon) and six unknown ferrosilicon samples were performed using only the sodium hydroxide fusion flux. The average percentage silicon, which was calculated using equation (1.5), as well as the average and standard deviation for the NBS standard and each of the unknown ferrosilicon samples is shown in Table 1.10. This table lists the number (N) of analysis performed, the average percentage of silicon present in each sample as well as their corresponding standard deviations. The average percentages of silicon in the NBS and unknown ferrosilicon samples one through six were 75.07, 47.90, 30.20, 47.75, 75.51, 51.51, 16.04 percent respectively. Table 1.10 also lists the standard deviations (in % Si) for each of the above mentioned ferrosilicons as .18, .32, .19, .19, .29, .36 and .19 percent.

A point of interest concerning the standard deviations is that there is one group (i.e. the NBS and unknowns 2,3 and 6) that fall within a range of between .1 to .2 percent and the other group (unknowns 1,4 and 5) have a higher standard deviation value of about .3 percent silicon. The only obvious difference between the

samples in these two groups was their particle size. The former had a finer particle size whereas the latter had a coarser particle size. The larger particles had a smaller surface area for reaction with the flux. Hence, some of the ferrosilicon in these samples may not have reacted completely, explaining the larger standard deviation.

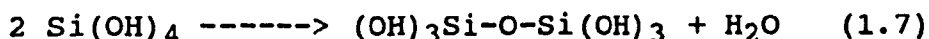
The criterion for the rejection of a suspect result, used in this work, was the "3.3 s rule". This rule provides a 99.9% probability that the rejection of the suspect result is valid. The values rejected using this rule were denoted by an asterix (\*). Of course, any result where a determinate error was observed, during the analysis, was rejected prior to performing the statistical analysis.

In this work the fused melt, which was the product of the fusion of the ferrosilicon with sodium hydroxide, was quantitatively transferred employing a glass stirring rod and rubber policeman with intermittent rinsings with hot deionized water. The melt was then decomposed with the addition of hydrochloric acid and gentle heating. The perchloric acid was added once the decomposition was complete. At this point the product, which contained sodium silicates, was converted to silicic acid by the following general reaction:



Therefore, at this step the products present were various hydrated forms of silicic acid and sodium perchlorate, sodium chloride, iron perchlorate and iron chloride salts<sup>8</sup>.

The solutions were covered and evaporated slowly (for safety reasons this step was carried out in a perchloric acid fume hood), to avoid possible "bumping", until they were dry. Then they were heated carefully until thick white perchloric acid fumes were observed, ensuring the complete dehydration of the silicic acid to silicon dioxide<sup>8</sup>. The processes of evaporation followed by dehydration caused the formation of a "silica gel like" product by the following condensation polymerization reaction of silicic acid:



The "perchloric acid method" has been recommended by Myshlyaeva and Krasnoshchekov<sup>8</sup> for the dehydration step because the perchlorate salts have a fairly high solubility, hence, they can be washed from the silicates. Also the dehydration and separation of the silicic acid as  $\text{SiO}_2$  is "more complete" using perchloric acid than when using either hydrochloric or sulphuric acids. When

using the perchloric acid method a mixture of perchloric acid and another acid, usually either nitric or hydrochloric acids are used in succession. Therefore, this method was chosen for this work.

The silicates were filtered by gravity and the precipitate was washed successively with hot 5% HCl and hot deionized water to remove any remaining perchlorate salts. The filtrate and rinsings were collected. The evaporation and filtration steps were repeated as suggested by Hillibrand<sup>7</sup>. This extra step is suggested because if the silica is removed by filtering, the filtrate evaporated to dryness and the residue heated to acid fumes then the silica remaining in the second filtrate is negligible<sup>7,8,9,10,11</sup>.

The two filter papers and corresponding precipitates were combined in a platinum crucible. The platinum crucibles were heated in a flame and then in a muffle furnace (850 °C) to remove the carbon of the filter paper by "ashing it". The crucibles were cooled in a desiccator and weighed to a constant weight. If insufficient washing of the silicates was performed then perchlorate salts remained within the samples. Thus, when the ignition step was performed the sodium perchlorate salts exploded causing the loss of silicates and hence the rejection of that particular experimental result.

After the filtering step, the purity of the silicic acid was verified by treating each crucible with a small amount of sulfuric acid (i.e. 5 drops) and hydrofluoric acid (5 ml). The HF reacted with the silicon dioxide ( $\text{SiO}_2$ ) present forming the volatile compound silicon tetrafluoride ( $\text{SiF}_4$ ) and water as shown in equation (1.4) earlier.

Thus, knowing the weight of the crucible and contents before and after the HF treatment and re-ignition step allowed the calculation of the amount of silicon present in the sample to be performed. This calculation began by finding the difference of the two weights, as  $\text{SiO}_2$ , and then by using equation (1.5) the percentage of silicon in the ferrosilicon was found for each sample. Since the precipitate could have been contaminated, this treatment allowed the differentiation of the dehydrated silicic acid from many other possible insoluble or partly soluble substances. The possible contaminants that can be differentiated, because of their nonvolatile nature, when using the HF treatment include alumina, iron oxides, titania, carbides, graphite and tungstic acid<sup>8</sup>. The sulfuric acid was added to bind the water produced during the above reaction, thus, preventing the hydrolysis of the silicon tetrafluoride<sup>9</sup>,  
10.

A contaminant that has been experimentally difficult to differentiate, from the silicon dioxide, when employing the HF treatment is boron. If boron is present it can be volatilized as boron trifluoride ( $\text{BF}_3$ ) along with the silicon tetrafluoride giving false high results. However, boron is present in ferrosilicon in such a relatively small amount, as shown in Table 1.2, which was adapted from the ASTM ferrosilicon specifications<sup>11</sup>, that this was not expected to cause a significant error.



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## **2 THE ANALYSIS OF SILICON IN FERROSILICON USING AN ION CHROMATOGRAPHY METHODOLOGY**

### **2.1 INTRODUCTION TO ION CHROMATOGRAPHY**

In the late 1970's the term "ion chromatography" or IC was defined as a technique that employed both an ion exchange separation and an electrical conductivity cell as the detector. However, in the last ten years the IC definition has been broadened to include detectors other than conductivity including other electrochemical as well as spectrophotometric detectors. Thus, the definition of IC suggested by Jupille<sup>1</sup> as "the analysis for dissolved ions using liquid chromatography" may be the best description. Fritz, Gjerde and Polhandt<sup>2</sup> recommend that IC refer to the general term for "a process in which the ions are separated chromatographically for the purpose of their analysis". For simplicity, since most of the current literature still uses the first definition, in this work the older definition of IC as a HPLC separation method combined with conductivity measurement will be employed. However, mention will also be made to methods of detection other than conductivity measurement.

The literature has grouped IC techniques into two divisions. The first involves the use of an eluent modified system. The second division uses no system of

eluent modification. In the eluent modification division some chemistry is performed on the eluent and sample ions between the separator column and the detector.

The first division, the eluent modification methods, can be broken into two subdivisions which are the eluent modification by derivatization and by suppression. The eluent modification by derivatization methods include post-column reactions (PCR) where derivatization reagents are mixed with the eluent just prior to detection with either optical absorbance or fluorescence measurements. The second eluent modification system employs the chemical suppression of the background conductivity, when conductivity detection is employed, using a second column. This method was first introduced by Small et al.<sup>3</sup> and is called either the "suppressed" or "dual column IC" (DCIC) system. The DCIC system is unique to the Dionex company and was not used in this work. It will, however, be discussed briefly since it has become an important application in IC.

Some of the earliest methods developed for IC had a serious flaw. This flaw occurred because the sensitivity of the electrical conductivity detector, connected directly to the separator column, was dependent on the difference between the equivalent conductances of the sample and buffer (present from the eluent) ions. In

situations where the sample and buffer ions had similar equivalent conductances the results showed poor sensitivity, since there was only a small change in the background conductance as the sample ions replaced the buffer ions. These techniques included the use of sodium bicarbonate and sodium carbonate eluents to separate strong acid ions such as nitrate, sulfate and chloride. Since the equivalent conductances of these eluents are relatively close to those of the inorganic ions being separated, the sensitivities were low<sup>4</sup>.

The DCIC technique developed in the 1970's by Small, Stevens and Bauman<sup>3</sup> improved the overall sensitivity by chemically changing the column effluent after the separation of the ions by the separator column. When performing anion-exchange chromatography they passed the effluent through a cation-exchange resin in the hydrogen or proton form. This removed the sodium ions from the effluent and replaced them with hydrogen ions, hence, decreasing the conductivity. The result of this process was the conversion of sodium carbonate (high-equivalent conductance) to carbonic acid (low-equivalent conductance). Also, once the sample ions passed through the suppressor column, they were converted to a more highly conductive form. If samples of sodium chloride, sodium sulfate and sodium nitrate are passed through the

suppressor column then hydrochloric, sulfuric and nitric acids would be obtained. The overall effect was to amplify the differences of the equivalent conductances of the sample and buffer ions. This decreased the overall background conductivity and increased the signal. Therefore, the signal to noise ratio ( S/N ) was enhanced. The literature lists a great deal of research using the suppressed system<sup>3,5,6,7,8,9,10,11,12,13,14</sup>.

The second division is called the "nonsuppressed" or "single column IC" (SCIC) and this type of technique was first introduced by Fritz, Gjerde and Schmuckler<sup>15,16</sup> . This system only employs one column, hence, the term "single column". Here the detector is connected directly to the separator column. The most common form of apparatus available involves the direct coupling of an electrical conductivity detector to an ion-exchange column. The separator column is packed with a low capacity ion-exchange resin. The separator column and eluent are carefully chosen to provide both good separation of the ions of interest and a low background conductivity. When the eluent provides a low background conductivity the suppressor column is no longer required and can be eliminated. This, of course, is the basis of the SCIC technique. The literature lists many determinations using SCIC<sup>15,16,17,18,19,20,21,22,24</sup>.

In this work, the determination of silicon in ferrosilicon using SCIC, sodium silicates are produced from the original ferrosilicon compounds by fusing them with a sodium hydroxide fusion flux. The separation of the silicates, from any possible interfering anionic compounds also present, is performed using a low capacity anion-exchange separation column, since the silicate is present as a negatively charged species. In fact, in this instance the specific term of "anion chromatography" could be used to describe the process.

Since the instrumentation available to this author was a Waters SCIC system, the rest of this work will deal with the theory of SCIC anion chromatography as well as with the specific application for the analysis of silicon in ferrosilicon using this technique.

#### **2.1.1 BASIC INSTRUMENTATION FOR ANION CHROMATOGRAPHY USING SCIC**

In 1978 a simple chromatographic methodology was developed by Fritz et al.<sup>5,6</sup> that allowed for the rapid separation of some common anions. Their system used a low capacity anion-exchange separator column connected directly to a conductivity detection cell. In this instance a suppressor column was not required because of two developments: (1) the eluents adopted for

separation had a very low conductivity, and (2) a special low capacity anion-exchange resin (0.007 to 0.04 mequiv./g) was employed. The eluents used included potassium, ammonium and sodium salt solutions of phthalate, o-sulfobenzoate and benzoate in the concentration ranges of  $1.0 \times 10^{-4}$  M to  $5.0 \times 10^{-4}$  M. They obtained very sharp separations of the anions, employing the above mentioned conditions, without the use of a suppressor column.

Their new system was called SCIC and an example of a schematic representation of the apparatus is shown in Fig. 2.1.



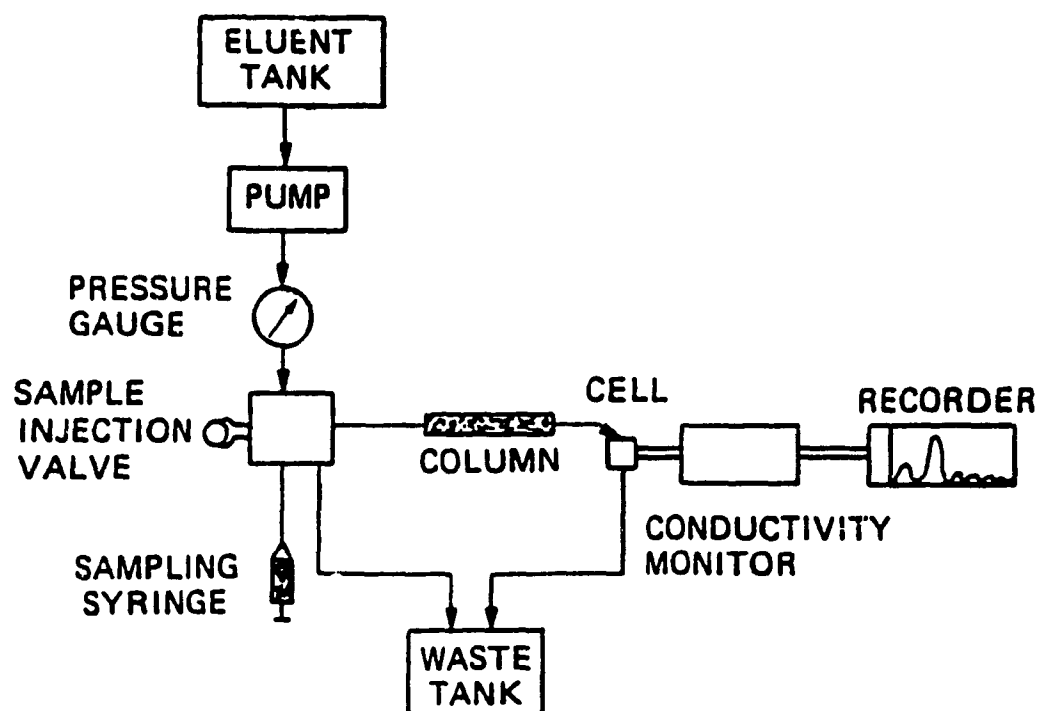


Fig. 2.1 A schematic representation of the SCIC apparatus

Their apparatus consists of the following components: (1) the pump which forces the eluent through the column, sample loop and conductivity cell at flow rates of 0.8 to 2.0 ml/min; (2) the sample injection valve, made up of a 100 microliter sample loop, enabling the reproducible introduction of 100 microliters of sample; (3) the anion-exchange separator column which was approximately 50 cm long and had an internal diameter of 2-3 mm. The small and uniform particle size resin was synthesized, by the authors, from Rohm and Hass XAD-1 to provide a capacity of 0.007 to 0.04 mequiv./g <sup>2,15,16</sup>; (4) the conductance of the column effluent was continuously monitored by an electrical conductivity cell coupled to a conductance detector; (5) an integrator or recorder was used to trace the conductivity versus time chromatogram.

#### 2.1.2 ANION-EXCHANGE EQUILIBRIA

An ion-exchange equilibrium involves the substitution of one ionic species for another. This involves the exchange of ions between the mobile and stationary phases. In the case of anion-exchange a sample anion is exchanged for the eluent anion or vice versa. The exchange of a monovalent anion, between a solution and an active site on the solid anion-exchange resin, can

be represented generally by the following expression:



The anion  $B^-$ , that is originally in solution, binds to the anion-exchange site on the resin which in turn displaces anion  $A^-$  from the site and into the solution. For anion-exchange processes the active sites on the resin surface or stationary phase carry a net positive charge which will attract and bind the anion.

This means that a "buffer" or eluent anion is liberated from the stationary phase every time a sample anion is bound to a site on the stationary phase. Of course the opposite is also true, that a sample anion is liberated from a site on the stationary phase every time a buffer anion binds to that site. Thus, it may be stated that the overall concentration of the anions in the column effluent remains constant; however, the identity of the the anions present can change due to the anion-exchange processes.

The case of a multivalent anion-exchange process can be represented generally by the following expression:



In either the multivalent or monovalent case an equilibrium exists which can be represented by its corresponding equilibrium constants or " selectivity

coefficients ". The selectivity coefficients (represented by K) for both the general expressions of the monovalent and multivalent cases, can be respectively represented by equations (2.3) and (2.4):

$$K = [\text{BR}] [\text{A}^-] / [\text{AR}] [\text{B}^-] \quad (2.3)$$

$$K = [\text{BR}]^a [\text{A}^-]^b / [\text{B}^-]^a [\text{AR}]^b \quad (2.4)$$

The anion concentrations are usually stated in mmoles/g in the case of the stationary or resin phase and in mmoles/ml for the mobile or solution phase.

### 2.1.3 THE SEPARATION COLUMN AND ANIONIC RESINS

The conventional anion-exchange resins are simply prepared from styrene-divinylbenzene (S-DVB) copolymeric beads by chloromethylation. They are then reacted with an amine to form the anion-exchange sites<sup>2</sup>. However, in most instances high capacity anion-exchange resins are formed because most of these types of resins react completely. If such high capacity anion-exchange resins are used, in packing separation columns, problems are encountered. The speed of the separation is limited by the diffusion of the anion into and out of the resin bead as well as the exchange reactions occurring with the anionic exchange sites<sup>4</sup>. An overall lack of efficiency is observed because of zone

dispersion and slow mass transfer. Hence, this type of anion exchange resin is not practical as a separator column packing for SCIC work.

The separator columns used in cation-exchange IC are packed with pellicular resins usually made from styrene-divinylbenzene (S-DVB). This type of resin has a low capacity. A pellicular resin has its active capacity (i.e. cation-exchange sites) at the surface of the bead. Therefore, the internal volume into which the ions can diffuse is minimized, increasing the efficiency.

The low capacity cation-exchange bead is analogous to a billiard ball covered with a thin layer of gelatin. The active sites of the resin are contained on the thin surface of the gelatin layer. The surface shell is swollen and porous, allowing the mobile phase to flow in and out easily.

The anion separator column packing is made up of two types of resins combined in one bead. In fact, the previously mentioned surface-sulfonated S-DVB resin used in cation-exchange separator columns is the starting substrate for the low capacity anion-exchange separator resin used in SCIC work. The surface of the surface-sulfonated S-DVB substrate is coated with an

aminated latex to create the required anionic sites for the anion separator resin. This type of resin, which was created originally by Dionex, was made by attaching a microparticle aminated latex to the surface-sulfonated resin. The fine particles of the latex electrostatically attach themselves to the surface of the resin, forming a thin second layer. This patented process called "agglomeration" yielded a highly efficient anion separator column packing. Representations of this type of resin as well as a conventional anion-exchange resin are shown in Figs. 2.2 and 2.3.

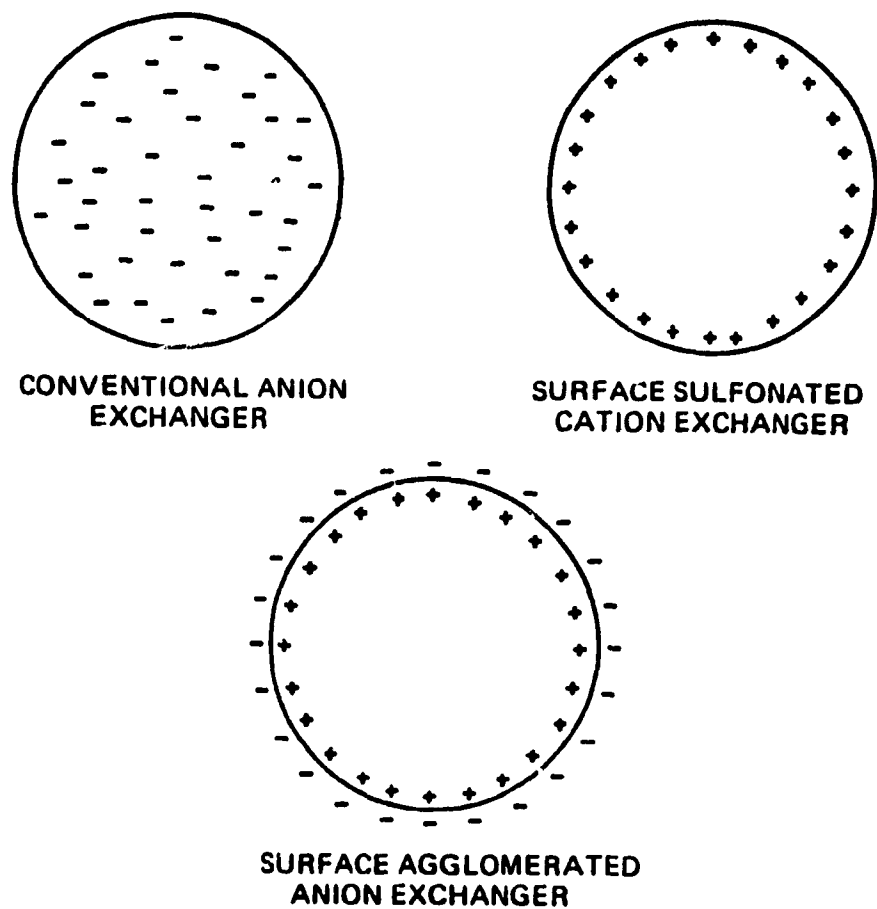
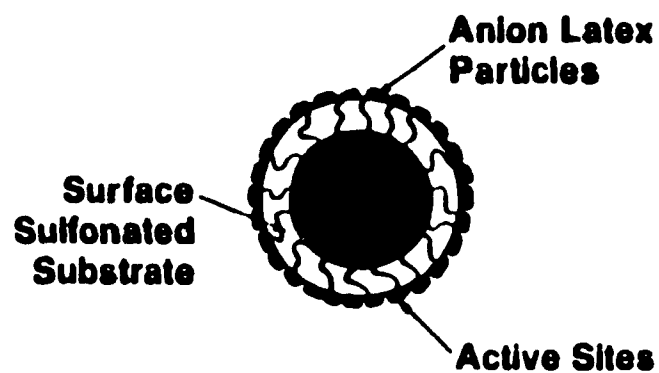


Fig. 2.2 A representation of the conventional anion exchanger, the surface sulfonated cation exchanger and the surface agglomerated anion exchanger.

# ANION SEPARATOR



## Anion Pellicular

# LATEXED ANION EXCHANGE PARTICLE

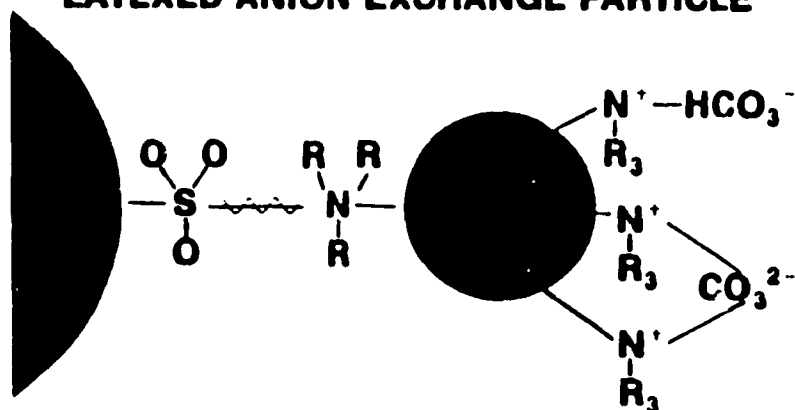


Fig. 2.3 An IC anion separator resin.



As mentioned earlier, the latex adheres to the surface primarily by electrostatic forces. That is, the positively-charged latex particles are attracted to the negatively-charged surface sites primarily by Van der Waals forces. This type of resin provides both good separation and sharp peaks as the result of excellent mass transfer and both low interstitial and low internal volumes<sup>4</sup>. Thus, the resin resulting from this treatment, has both a high selectivity and low capacity for anions. This in turn allows the use of an eluent having a low concentration (i.e. low background conductivity) but it still provides good separation of the anions present<sup>2</sup>.

An advantage of the pellicular resin anion-exchange columns is that they may be applied with high pH eluents to separate some weakly dissociated anions using SCIC combined with an electrical conductivity detector. This group includes silicate, borate, cyanide and sulfide<sup>2</sup>. The high pH eluent ensures that the sample species are ionized as well as providing the buffer anions. These types of resins also provide good sensitivity. The pellicular resins are also capable of providing efficient and rapid

separation of anions while withstanding the high pressures present in IC systems, resulting in long-column lifetimes.

#### 2.1.3.1 DISTRIBUTION COEFFICIENT

The two types of distribution coefficients often referred to in the literature are the weight or volume distribution coefficients. The weight distribution coefficient,  $D_g$  for the anion  $A^-$  is defined as the amount of  $A^-$  bound to the resin divided by the amount in solution:

$$D_g = [A^-]_r / [A^-]_s \quad (2.5)$$

$D_g = (\text{mmoles of } A^-) (\text{ml solution}) / (\text{mmoles of } A^-) (\text{g of resin})$

The volume distribution coefficient,  $D_v$ , has been used by some authors and is related to  $D_g$  by the following equation:

$$D_v = (D_g)(\rho) \quad (2.6)$$

where  $\rho$  is the density

The weight distribution coefficient,  $D_g$ , of an anion  $A^-$  in a specified eluent may be calculated experimentally by equilibrating a known weight of resin with a known volume of standard solution and then using equation (2.5). The volume distribution

coefficient,  $D_V$ , of an anion  $A^-$  is calculated from its retention volume ( $V$ ) upon elution with a specified eluent from a small anion-exchange column. This process is represented by the following equation:

$$V = D_V + 1 \quad (2.7)$$

It must be mentioned, however, that this method does not work if the conditions are such that  $D_V$  is very large<sup>2</sup>. Also, in general, the affinity of an anion-exchange resin increases with an increase in the charge of the anion.

#### 2.1.3.2 CAPACITY FACTOR

Often in IC work the authors have found it convenient to use a value called the "capacity factor" instead of the distribution coefficient. The capacity factor, which is sometimes referred to as the "mass distribution ratio", of an anion is the amount (but not the concentration) bound to the resin phase of the column divided by the amount present in the solution. When substituting this definition into equation (2.5), the following relationship is obtained:

$$D_g = (k) \text{ volume solution (ml) / weight resin (g)} \quad (2.8)$$

$$k = (D_g) \text{ weight resin (g)/volume solution (ml)} \quad (2.9)$$

These equations indicate that the capacity factor may be found from the distribution coefficients that are obtained by the equilibration of the resin with an anion present in the ionic solution.

In HPLC work, however, it is usually more convenient to find the capacity factor from the retention volume ( $V$ ) or the retention time ( $t$ ) of the eluted anion. To use this procedure requires that either the "dead time" ( $t_0$ ) or the "dead volume" ( $V_0$ ) of the column be known. These values are obtained by simply measuring the volume or time for an anion that is not retained by the resin. Then the capacity factor is found by using one of the following equations:

$$k = (V - V_0) / V_0 \quad (2.10)$$

$$k = (t - t_0) / t_0 \quad (2.11)$$

#### 2.1.4 CHROMATOGRAPHIC PSEUDO PEAK

Before performing a series of injections of samples the eluent is pumped through the IC system until an equilibrium is attained where the exchange sites on the resin are bound by the eluent anion. This produces a constant background conductance which is

taken as the baseline.

Once a sample, containing various anions, is injected onto the column they will be removed from the solution by binding to the exchange sites on the resin and they will also replace an equivalent amount of the eluent anions previously bound to those same sites. The unretained ions (including cations) are carried, as a zone, down the column and to the detection cell at the same speed as the eluent flow rate.

The zone is composed of two types of ions: the equivalent amount (i.e. equivalent to sample anions displacing them) of the displaced eluent anion and the unretained cations that are present in the original sample. When this zone passes through the detector it causes a change in the baseline conductance producing a peak. This peak is referred to as the "pseudo" or "system" peak. The pseudo peak is often an obstacle since it may overlap with the peaks of interest. It is often difficult to resolve them especially if the retention times of the solute peaks are small.

The pseudo peak obtained can be either negative or positive depending on the overall change in conductance at the detector. If the conductance of the zone is lower than the background conductance of the eluent a

negative pseudo peak is observed. If the conductance of the zone is higher than the background conductance of the eluent then a positive pseudo peak is observed.

#### 2.1.5 CHROMATOGRAPHIC SAMPLE PEAKS

After the pseudo peak has passed through the detector, the eluent baseline or background conductivity is restored to its initial value. The sample anions are moved gradually down the anion-exchange column by the "mass action effect" of the eluent anion on the sites of the anion-exchange resin. The total cation concentration is constant and fixed by the eluent cation concentration. The sample anions only enter the mobile phase by the uptake of an equivalent amount of eluent anions, thus, the change in conductance when the solute band passes through the detector results from the displacement of the eluent anions by sample anions. Although a change in conductance occurs, the total ion concentration remains constant, but the identity of the anion changes. The observed change in conductance is directly proportional to the difference in the equivalent conductances of the eluent and sample anions and is a function of the original sample anion concentration.

The sample ion species are detected relative to the constant background conductivity or baseline. The peak for each anion present is recorded on the chromatogram. The chromatogram is simply a plot of conductance versus the characteristic elution time or retention time of each anion. Normally in anion IC work the background signal of the eluent is lower than the sample ion signal, resulting in a positive electrical conductance reading, observed as a peak. However in this work the background signal is greater than the sample signal resulting in a decreased or negative conductance peak. Hence, the mobile hydroxide eluent anion had a larger equivalent conductance than the silicate anion so a negative peak was obtained.

#### 2.1.6 RESOLUTION

A problem that is encountered frequently in IC analysis involves the overlapping of two or more peaks in the chromatogram. To obtain meaningful analytical results requires that one is capable of resolving the peaks entirely. This serious problem can be minimized, in a variety of ways, to improve the anion separations and hence the overall resolution. The alternate methods employed consist of: (1) a simple dilution or a chemical pretreatment of the sample; (2) the use of a

different eluent concentration (i.e. the lower the concentration the higher the resolution); (3) the use of a longer separator column; (4) changing the type of separator column; (5) the use of a different ion separation mechanism. Each of these methodologies can be employed to increase the resolution of a chromatogram<sup>4</sup>.

#### **2.1.7 DETECTORS FOR ION-EXCHANGE SEPARATIONS**

There are many different types of detectors, other than conductivity, that can be employed in ion-exchange separations using HPLC (High Performance Liquid Chromatography). As mentioned earlier these detection methods combined with HPLC are often referred to as IC. The major detectors used in ion chromatography are listed in Table 2.1. These alternative detection methodologies include refractive index and spectrophotometric detection techniques such as ultraviolet-visible; spectrometric detectors such as atomic absorption and flame emission; electrochemical detection techniques including amperometry and coulometry.

Although there are many alternative detection techniques, they can all be classified as either selective or universal detectors. A universal detector responds to any and all the ions present in the



solution, whereas a selective detector responds to only specific ions found in the detection cell. In the case of the selective detector the eluent can be chosen so as not to give a response. The U.V. detection method is an example of a selective detector since there is no response due to the eluent and the only absorption response is due to the chromaphoric group present on the sample ion. An example of a universal detector is a conductivity detector because all the ions in the solution will conduct<sup>2</sup>.

**TABLE 2.1****DETECTORS USED IN ION CHROMATOGRAPHY**

<b><u>Detectors</u></b>
Conductivity, suppressed
Conductivity, SCIC
Spectrophotometric
Fluorimetry
Refractive index
Electrochemical
Atomic absorption
Atomic emission

#### 2.1.7.1 IC DETECTION

The conductivity detector measures the ability of a solution to conduct electricity. The conductance is proportional to the number of ions in the solution as well as their respective mobilities. In this section both detection principles and the equations describing conductance itself will be discussed.

The electrolytic conductivity can be defined as the ability of an electrolytic solution to conduct electricity across two electrodes that have an electric field applied between them. Ohms law can be applied in this instance, thus, the magnitude of the current (I) is dependent upon the applied potential (V) as well as the electrolytic resistance (R) provided by the solution in the cell:

$$V = IR \quad (2.12)$$

The conductance (G) of the solution is expressed in terms of its electrolytic resistance:

$$G = 1/R \quad (2.13)$$

The units of electrical conductance can be stated as either  $\text{ohm}^{-1}$  or mho or microsiemens ( $\mu\text{mho}$ ).

The specific conductance ( $k$ ) is a measure of the conductance with respect to the distance ( $L$ ) between the electrodes ( $\text{cm}$ ) and the area ( $A$ ) of the electrodes ( $\text{cm}^2$ ) and its units are  $\text{mho cm}^{-1}$ :

$$k = G L/A \quad (2.14)$$

The cell constant ( $K$ ) is defined as the distance between the electrodes divided by the area of the electrodes:

$$K = L/A \quad (2.15)$$

Therefore equation (2.14) can be rewritten as:

$$k = GK \quad (2.16)$$

The chemical concentration of the solution is accounted for by the equivalent conductance ( $\Lambda$ ) which is defined as one thousand times the specific conductance ( $k$ ) divided by the concentration ( $C$ ) in equivalents per 1000  $\text{cm}^3$ :

$$\Lambda = (1000) \frac{(k)}{(C)} \quad (2.17)$$

By combining equations (2.16) and (2.17) an equation is obtained that relates the measured conductance ( $G$ ) to the equivalent conductance ( $\Lambda$ ) :

$$G = \frac{(\Lambda C)}{(1000 K)} \quad (2.18)$$

#### **2.1.7.2 THE PRINCIPLES OF THE OPERATION** **OF A CONDUCTANCE CELL**

In an electrolytic solution, cations will move towards the cathode and anions will move towards the anode, when an electric field is applied between the two electrodes. The resistance of the solution (i.e. reciprocal conductance) is determined by both the velocities and the number of ions in the electrolyte. The ionic mobility is defined as the velocity per unit of potential of the electric field. The ionic mobility is dependent on the size and charge of the ion. The ionic mobility is also dependent on the ionic concentration, medium and the temperature<sup>2</sup>. The ionic limiting equivalent conductances ( $\lambda$ ) are often used to represent the relative mobility of an ion. Tables of the ionic limiting equivalent conductances are available in the literature<sup>2,4</sup>. The velocity of the ion is dependent on the magnitude of the applied potential. This potential can be either constant or it can oscillate as a pulse square wave or a sinusoidal wave.

The cell resistance is determined by applying a potential to the cell and measuring the current. However, the effective applied potential to the cell can be varied by other ionic behavior as shown in

Fig. 2.4. Other than the electrolytic resistance phenomena both the double layer capacitance and Faradaic impedance cause the effective potential of the cell to change. Both of these phenomena will be discussed briefly below.

When an electrode is below its decomposition potential it attracts ions of the opposite charge, from the solution layer immediately adjacent to it, and a charged double layer is formed. The double layer consists of two very different regions. The first region consists of a thin layer of oppositely (opposite to the electrode) charged ions. In this region the ionic concentration or potential decreases linearly with the distance from the surface of the electrode. The second region consists of a diffuse layer where the ionic concentration decreases exponentially. The formation of the double layer capacitance lowers the effective potential applied to the bulk of the electrolyte<sup>2</sup>.

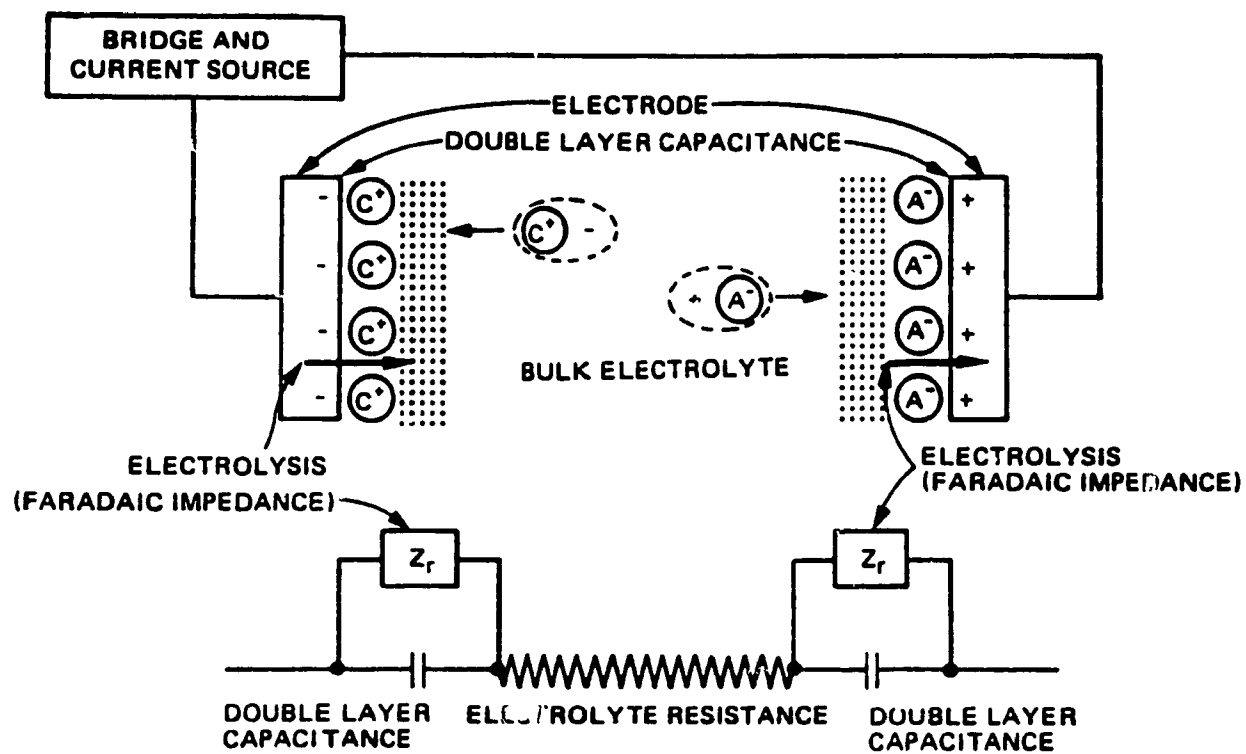


Fig. 2.4 Processes that occur in an electrolytic conductance cell.

A process called electrolysis will occur if the applied potential is larger than the decomposition potential. In electrolysis the current flows across the interface of the electrolytic solution and the surface of the electrode by reduction at the cathode and oxidation at the anode. A buildup or depletion of ions at the electrode surface, or slow electron transfer processes, can result in Faradaic impedance. The Faradaic impedance can also alter the effective potential applied to the bulk electrolyte<sup>2</sup>.

#### 2.1.7.3 PERFORMING CONDUCTANCE MEASUREMENTS

The conductance measurement can be simplified by eliminating both electrolysis and the double capacitance formation at the electrode surface. The techniques used, to eliminate these phenomena, are either the alternating electrode potential or bipolar pulse conductance methods.

The bipolar pulse conductance technique involves the sequential application of two short duration (approx. 100  $\mu$ sec) voltage pulses to the conductance cell. The pulses have opposite polarities, however, they have equal duration and magnitude. At the precise time that the second pulse ends the cell current is measured. The cell resistance can then be



determined using Ohm's law. The bipolar pulse conductance technique prevents electrolysis from occurring<sup>2</sup>. Since the bipolar pulse conductance technique measures an instantaneous cell current the formation of a double layer capacitance has not occurred, hence, it is no longer a problem.

The alternating electrode potential technique can also be used to eliminate these electrode processes. By changing the sign of the potential applied to the electrode the direction of the ion migrations are reversed, altering the processes of the capacitance formation and electrolysis<sup>2</sup>. By increasing the frequency of the switching of the sign of the charge on the electrode the process of electrolysis is eliminated, thus, the ions no longer move in response to the electric field. The capacitance effects can be eliminated by measuring the instantaneous current as mentioned above. The instantaneous current is taken just prior to the application of the third pulse (i.e. immediately after the second pulse), therefore, the double layer has not had time to form and there is no capacitance involved.

#### 2.1.8 SENSITIVITY

In SCIC the relative sensitivities of different methods are compared using the change in conductance caused by the replacement of the eluent anion with the sample anion. Fritz et al.<sup>2</sup> have taken the approach of utilizing the limiting equivalent conductances ( $\lambda$ ) of various cations and anions to calculate the expected baseline conductance for different eluents. They then compared their calculated values against the observed values for the baseline conductances. They stated that the calculated and experimentally observed values "showed quite reasonable agreement"<sup>2</sup>.

Their approach involved calculating the cell constant ( $K$ ), using equation (2.16), where  $k$  was the known specific conductance of the eluent and  $G$  was the observed conductance. They then measured the observed conductances ( $G$ ) of several different eluents and knowing their specific conductances ( $k$ ) they were able experimentally to find their cell constant to have a value of  $33.0 \text{ cm}^{-1}$ .

Using the literature values for the limiting equivalent conductances ( $\lambda$ ) they calculated the expected conductance ( $G$ ) using equation (2.19):

$$G = \frac{((\lambda_+ + \lambda_-)(C)(i)(10^6))}{(10^3 K)} \quad (2.19)$$

where  $\lambda_+$  is the limiting equivalent conductance of the cation and  $\lambda_-$  is the limiting equivalent conductance of the anion,  $K$  is the cell constant,  $i$  is the fraction of the eluent that is ionized and  $C$  is the concentration (normality) of the eluent. The term is divided by  $10^3$  to convert  $\text{cm}^3$  to  $\text{dm}^3$  (or liter). The factor of  $10^6$  converts the measured conductance ( $G$ ) to  $\mu\text{mho}$ .

They found that the accuracy of the calculated and experimental results were limited by the following factors: (1) imprecise temperature control; (2) use of the limiting equivalent conductances ( $\lambda$ ) instead of the equivalent conductances ( $\Lambda$ ) at the concentrations employed; (3) a somewhat limited accuracy when measuring the cell constant<sup>2</sup>.

#### 2.1.8.1 THE CONDUCTANCE OF A SAMPLE PEAK

When employing the technique of ion chromatography an important point to keep in mind is that the overall concentrations of both the cations and anions, present in the eluent, is constant and this makes up most of the baseline conductivity (but there is also an inherent background noise present). Hence,

the overall background conductance is constant and only changes upon elution of a sample anion off the column and through the detector.

The concentration of the eluent anion  $E^-$  is decreased when a sample peak elutes by  $C_E - (C_S i_S)$ . If we substitute this into equation (2.19), the value for the conductance ( $G$ ) when a peak is eluting can be found. The change in the measured conductance ( $G$ ), when a sample anion is present in the conductance cell, can be calculated using equation (2.20), shown below:

$$G_s = \frac{\{(\lambda_{E^+} + \lambda_{E^-})(C_E - C_S i_S) i_E\}}{(10^{-3} K)} + \frac{\{(\lambda_{E^+} + \lambda_{S^-}) C_S i_S\}}{(10^{-3} K)} \quad (2.20)$$

where  $C_S$  = the concentration of the sample anion  $S^-$ ,  $C_E$  = the concentration of the eluent anion  $E^-$ . Also  $E^+$  represents the eluent cation and  $E^-$  represents the eluent anion. The symbols  $i_S$  and  $i_E$  represent the fraction of the sample or eluent that are ionized respectively

When there is no sample present in the cell, the equation for the baseline conductance ( $G_B$ ) is shown below:

$$G_B = \frac{\{(\lambda_{E^+} + \lambda_{E^-})(C_E i_E)\}}{(10^{-3} K)} \quad (2.21)$$

Subtraction of equation (2.21) from (2.20) gives the change in conductance ( $\Delta G$ ) when a peak is eluted :

$$\Delta G = G_s - G_e \quad (2.22)$$

or

$$\Delta G = \left\{ (\lambda_{e-} + \lambda_{s-}) i_s - (\lambda_{e-} + \lambda_{e+}) i_e i_s \right\} \frac{C_s}{(10^{-3} K)} \quad (2.23)$$

Equation (2.23) shows the relationship between the sample concentration and the response of the detector. The cell constant ( $K$ ) and the limiting equivalent conductances remain constant under most conditions. The values of  $i_E$  and  $i_S$  are dependent on the eluent concentration, the pH, and the  $K_a$  of the respective acid.

Fritz<sup>2</sup> makes the assumption that  $i_E$  and  $i_S$  are equal to 1, therefore, equation (2.23) was simplified to:

$$\Delta G = (\lambda_{s-} - \lambda_{e-}) \frac{C_s}{(10^{-3} K)} \quad (2.24)$$

Thus, the change in conductance ( $\Delta G$ ) is directly proportional to the differences in the equivalent conductances of the eluent and sample anions.

In SCIC if the sample anion has a higher equivalent conductance ( $\lambda$ ) than the eluent anion the

overall conductance peak is positive (i.e. an increase in the total conductance). If the sample anion has a lower equivalent conductance than the eluent anion the conductance peak is negative (decrease in the total conductance).

## **2.2 EXPERIMENTAL SECTION**

### **2.2.1 MATERIALS AND REAGENTS**

The eluent was prepared daily by dissolving reagent grade sodium hydroxide (ACP Chemicals inc.) in previously boiled deionized water. The eluent was deaerated using vacuum. The metasilicate standard solutions were prepared by diluting a previously prepared stock solution (1000 ppm) of reagent grade sodium metasilicate (Baker and Adamson Chemical Co. Ltd.)  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ .

The NBS ferrosilicon standard and unknown ferrosilicon samples were fused (10:1 ratio) using reagent grade sodium hydroxide and a blank was prepared with each run. The samples were heated under pressure using a Presto pressure cooker and filtered using Whatman # 42 ashless filter paper. The filtrates from the two filtering steps for both the stock NBS standard and unknown solutions were combined and stored in 1L Nalgene (polymethylpentene PMP) transparent plastic volumetric flasks.

### **2.2.2 INSTRUMENTATION**

A Waters 6000A pump and a U6K Waters injector were combined with a Waters 430 conductivity meter as the

nonsuppressed ion chromatograph system in this work. A Waters anion guard column (p/n 07357) was connected just prior to the analytical separator column to protect it from blockage and the resulting pressure build up inherent to this problem. The anion-exchange separator column employed was a Hamilton PRP-X100 column, which had been used in the analysis of silicates by Lee<sup>22</sup>. The chemical and physical characteristics and the specifications of the PRP-X100 anion exchange column are shown in Tables 2.2 and 2.3 respectively.

The flow rate was maintained at 2.0 or 2.5 mls per minute under a pressure of 3.5-4.5 KPsi. The samples were injected using a 100 microliter ( $\mu$ l) Hamilton syringe. A HP integrator (3392A) was used to perform the integration of the conductivity detector electrical signal (i.e silicate peak), providing the corresponding area. The parameters used in this IC work are shown in Tables 2.4 and 2.5 for the metasilicate and NBS standards respectively.

The cell constant for the Waters 430 conductivity cell was found, using the conventional method of measuring the conductance of a standard KCl solution. In this instance the eluent ( [KCl] = 0.09998 M) was pumped through the SCIC system until a consistent value



for the conductance (  $1546 \mu S$  ) was obtained. The cell constant (K) was then calculated as  $9.67 \text{ cm}^{-1}$  using equation (2.18) where  $\Lambda = (\lambda_r) + (\lambda_a)$ . This experimental value was in agreement with the value stated by Waters as  $10 \text{ cm}^{-1}$  nominal.

**TABLE 2.2**  
**THE CHEMICAL AND PHYSICAL CHARACTERISTICS**  
**OF THE PRP-X100 SEPARATOR COLUMN**

void volume	0.65 ml/min.
composition	poly(styrene-divinylbenzene) copolymer with trimethylam- monium exchange groups
particle size	10 micron spherical
exchange capacity	0.19 meq/g
pH range	1-13
temperature limit	5-60 °C for pH<7 ; 5-30 °C for pH>8

**TABLE 2.3**  
**THE SPECIFICATIONS OF THE PRP-X100**  
**SEPARATOR COLUMN**

column dimensions	250 x 4.1 mm i.d.(p/n: 79433)
efficiency	> or = to 16,000 plates/meter *
capacity factor (k)	4.5 for nitrite
column materials	316 stainless steel
end fittings	CPI-type (Parker and Hannifin)
pressure rating	5000 psi
maximum eluent flow rate	8.0 mls/min.

\* This was measured by Hamilton using the nitrite peak with a mobile phase of 4 mM p-hydroxybenzoic acid/ 2.5% methanol at a pH of 8.5 (adjusted with NaOH) and a flow rate of 2.5 ml/min.

**TABLE 2.4**  
**THE IC PARAMETERS USED IN THE SODIUM METASILICATE**  
**VERSUS FERROSILICON SAMPLES WORK**

eluent concentration	0.8-3.0 mM NaOH
eluent flow rate	1.0-3.0 ml/min.
eluent background conductance	200-600 microsiemen
pump pressure	3000-4500 psi *
detector gain	0.2
detector range	50 (x 10 microsiemen)
detector full scale	100 microsiemen

\* when the pump pressure reached about 4.0 Kpsi, the precolumn was separated from the PRP-X100, inverted, and rinsed with the solvent to remove any blockage particles.

**TABLE 2.5**

**THE IC PARAMETERS USED IN NBS STANDARD**  
**VERSUS UNKNOWN FERROSILICON SAMPLES WORK**

eluent concentration	0.8-3.0 mM NaOH
eluent flow rate	2.0 or 2.5 ml/min.
eluent background conductance	200-600 microsiemen
pump pressure	3000-4200 psi *
detector gain	0.2, 0.5 or 1.0
detector range	50 or 20 (x 10 microsiemen)
detector full scale	20, 25 or 40 microsiemen

\* when the pump pressure reached about 4.0 Kpsi, the precolumn was separated from the PRP-X100, inverted, and rinsed with the solvent to remove any blockage particles.

### **2.2.3 METHODOLOGY FOR THE ANALYSIS OF SILICON IN FERROSILICON BY IC**

The procedure began by weighing .35 g or 1.0 g of either the unknowns or NBS standard ferrosilicon sample and 3.5 g or 10.0 g of NaOH (minimum amount of flux required) into a nickel crucible. The crucibles were covered with a loosely fitting crucible cover, to allow the evolved hydrogen gas to escape, and fused slowly while rotating the crucible in a hot bunsen burner flame. Once the hydrogen gas evolution was no longer evident (i.e. no yellow flame present) the crucible was placed in a muffle furnace (at 850 °C) for 20 minutes to complete the fusion.

Then 20 ml of hot water was placed in each crucible and its contents were quantitatively transferred from the crucible to a 600 ml beaker, using a stirring rod and rubber policeman. The crucible was rinsed with hot water five or six times, after mechanically removing as much of the crucible contents as possible. The rinsings (approx. 200 ml) and crucible contents were combined in the beaker.

The 600 ml beaker was covered and placed in a stainless steel pressure cooker which was heated on a hot plate for 30-40 minutes. This pressure and

temperature enhanced system provided the proper environment for the sodium silicates, formed during the fusion process, to remain soluble<sup>23</sup>. The silicate solutions were then removed and filtered (Whatman #42) immediately, using suction, then the remaining iron hydroxide precipitate was rinsed with hot water and the filtrate was collected and stored in a 1L plastic volumetric flask. The precipitate (mainly iron hydroxide and possibly some insoluble silicates) and filter paper were collected, placed in a Pt crucible and were burned consecutively in a bunsen burner flame and then in the muffle furnace to remove the carbon of the filter paper by ashing it.

The crucibles were removed from the furnace and cooled in the desiccator for 20 minutes. The crucible contents were quantitatively transferred to a beaker and 100 ml of water was added. Once again the beaker was placed in the pressure cooker for a period of 30-40 minutes. This step was repeated to ensure that any insoluble silicates present with the insoluble iron hydroxide, after the first filtration, were now in solution. The silicate solution was quantitatively transferred to a Buchner funnel, was filtered and rinsed with hot water. The filtrate and washings were collected in the filtration flask, cooled and added to

the 1L flask by quantitative rinsing of the filtrate flask into the 1L volumetric flask which was finally completed to volume.

The filter paper and remaining iron hydroxide precipitate was burned again in the muffle furnace (forming its oxide), cooled and weighed. Then either a HF treatment or atomic absorption was used to check if any silicates remained insoluble. Since atomic absorption is a faster method it was chosen for most of the analysis of the iron hydroxide-oxide for any possible remaining silicates.

#### 2.2.4 PRETREATMENT

The pretreatment developed in this work was a modified version of the procedure used by Okada and Kuwamoto<sup>24</sup> in the "Determination of Silicic Acid in Natural Water". This pretreatment involved passing known amounts of the NBS standard solution and unknown ferrosilicon samples through a cation-exchange resin in its protonated form. A blank was prepared with each set of unknown ferrosilicon samples as well. The NBS ferrosilicon standard solutions were prepared by pipetting various known amounts of the NBS stock solution onto a Dowex HCR (cat. # D-196) high capacity cation-exchange resin to remove the interfering cations



(Na, Fe etc...) present in the standard. The silicates were washed off the column by rinsing the resin with small portions (10 mls) of hot previously boiled deionized water and the effluent was collected in a 250 ml plastic Nalgene flask. The unknown ferrosilicon samples as well as the blank were treated in the same manner. The solutions were cooled and analyzed for the concentration of silicon, using IC. This technique required that the standards and unknowns be periodically checked to ensure that no losses of the silicate anion had occurred during the pretreatment.

A problem that was encountered, when the pretreatment was employed, was the formation of carbon dioxide gas as the unknown samples were eluted through the cation-exchange resin. The gas was identified as carbon dioxide using a Drager Werk carbon dioxide (1%) analysis kit. The gas caused the resin to lift, allowing the channeling of the sample through the resin. This caused losses of the silicates in the cation-exchange column.

In an attempt to identify the origin of the carbon dioxide gas as either adsorbed from the atmosphere, by the sodium hydroxide flux, or inherent to the ferrosilicon samples, a Leco Combustion Furnace was

used to burn the starting ferrosilicon samples. The results are shown in Table 2.13 (p.94). The implications of these results will be discussed later.

#### 2.2.5 ATOMIC ABSORPTION METHODOLOGY

Approximately 0.50 g of the precipitate iron oxide, remaining after either the first or the second filtration step, was weighed into a 250 ml beaker and was digested using 25 ml of 10% sulfuric acid, 10 ml of concentrated hydrochloric acid and 10 ml of 60% hydrogen peroxide. The mixture was allowed to react at low heat until it dissolved (note: often part of the samples didn't dissolve) and then the temperature was raised to boil off the remaining hydrogen peroxide. During the boiling step the samples were not boiled longer than one minute because continued boiling causes the silicon to precipitate. The samples were transferred, by quantitative rinsings with deionized water, to a 100 ml volumetric flask which was then completed to volume. Any remaining precipitate settled to the bottom of the flask. An NBS silicon (certified as 0.509%) in steel standard was also prepared following this methodology.

The amount of silicon present in the unknown iron oxide precipitate was obtained from a calibration plot

of concentration versus absorbance for three silicon standards (50, 75 and 100 ppm). The absorbance reading for the unknown was used to find its corresponding concentration of silicon by reading it off the standard plot. The standards were made by diluting a 1000 ppm silicon Fisher standard. An NBS steel standard ( i.e. silicon) was also checked versus the calibration plot to verify the validity of the graph. A sample of the results obtained, from the iron oxide present after the first filtration, are shown in Table 2.14 and the calibration plot of concentration versus absorbance is shown in Fig. 2.8 (pages 95 and 96 respectively).

### 2.3 RESULTS

The percentage of silicon, in the unknown ferrosilicon samples, was found by comparing them with standard solutions. The concentrations of silicon in the unknown ferrosilicon solutions were determined by a comparison with either sodium metasilicate (i.e. water glass  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) standard solutions (simply obtained by dissolving in water) or further NBS standard solutions (diluted from a NBS stock solution and pretreated exactly as unknowns). In either case the concentrations of the standards were plotted against their corresponding peak areas (represented either as the area of width at half

height (i.e.FWHM) or integrator counts). An example of the calibration plots for the sodium metasilicate and NBS ferrosilicon silicon standards are shown in Figs. 2.5 and 2.7 respectively.

The values for the concentration of silicon in the diluted unknown ferrosilicon samples were simply calculated, knowing the area, by reading their values off the "best fit" linear regression line of the standards. The result for the concentration of silicon present in the unknown was then obtained by multiplying by the dilution factor. An example of one day's results, for the average peak area etc..., of the sodium metasilicate or NBS ferrosilicon silicon standards and unknown ferrosilicon samples are shown in Tables 2.6 and 2.10. All the rest of the "raw data" is listed in the appendix. The results for the concentration of silicon, in the unknown ferrosilicon sample, obtained using metasilicate standards and the gravimetric comparison are listed in Table 2.7. The results for the concentration of silicon, in the unknown ferrosilicon sample, obtained using the NBS standards and the gravimetric comparison are listed in Table 2.11.

The validity of the individual 100  $\mu$ l injections were determined using either the " $\chi^2_{0.90}$ -test" or the "3.3s rule". If the questionable result was in a statistical

pool of greater than 11 results, the 3.3s rule was employed to determine whether rejection was required. If the questionable result was in a statistical pool of less than 11 results then the  $Q_{0.90}$ -test was used to determine the rejection criteria. When a result was deemed "rejected" the average and standard deviations were recalculated for that statistical pool of results.

**TABLE 2.6**

**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF INJECTIONS FOR THE SODIUM METASILICATE SILICON STANDARDS AND UNKNOWN #4 FERROSILICON (26/11/88)**

<u>concentration of silicon standard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integrator counts)</u>	<u>standard deviation</u>
50	6	5.604 E5	1.6 E4
100	4	1.167 E6	3.6 E4
150	5	1.595 E6	5.3 E4
200	5	2.184 E6	4.2 E4
250	4	2.637 E6	4.0 E4
unk. # 4 sample 1	4	2.561 E6	1.5 E4
unk. # 4 sample 2	5	2.697 E6	1.7 E5
unk. # 4 sample 3	4	2.540 E6	1.8 E5

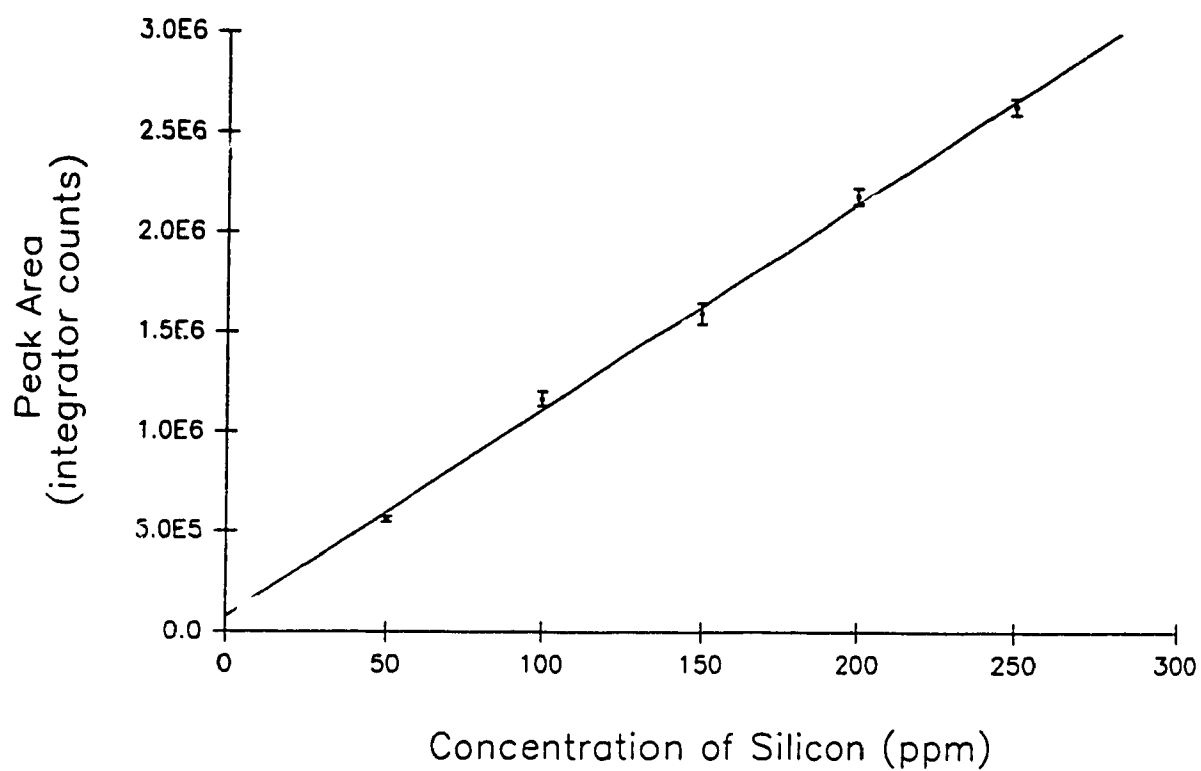


Fig. 2.5 The calibration plot of the average area of the silicate peak versus the concentration of silicon for the sodium metasilicate standards (26/11/88).

**TABLE 2.7**

**THE IC LINEAR REGRESSION LINE PARAMETERS FOR THE**  
**CONCENTRATION OF SILICON VERSUS THE PEAK AREA FOR**  
**THE METASILICATE STANDARDS AND THE RESULTS FOR**  
**THE CONCENTRATION OF SILICON IN THE NBS OR**  
**UNKNOWN FERROSILICON SAMPLES**

<u>date</u>	<u>number of stand- ards</u>	<u>slope</u>	<u>inter- cept</u>	<u>correl- ation coeff- icient</u>	<u>unknown ferro- silicon number</u>	<u>IC result for [Si] in the unknown or NBS ferro- silicon (ppm)</u>
19/11/88	5	9.69 E3	9.3 E3	.9989	#4	260.2
21/11/88	4	8.62 E3	1.1 E4	.9970	#4	274.7
24/11/88	4	9.76 E3	1.5 E5	.9999	NONE	NONE
25/11/88	3	9.69 E3	9.4 E4	.9998	#4	240.2
26/11/88	5	1.03 E4	7.8 E4	.9986	#4 #4 #4	240.1 253.4 238.2
1/12/88	4	9.88 E3	7.0 E4	.9983	NONE	NONE
2/12/88	3	1.15 E4	1.1 E4	1.000	#4 #4	247.6 260.7
9/12/88	4	1.06 E4	6.9 E4	.9999	NBS NBS	261.4 276.2
11/12/88	3	1.05 E4	1.2 E5	.9991	NBS NBS #4	243.5 245.8 248.0
15/12/88	3	1.07 E4	1.8 E4	.9999	NBS NBS NBS	239.3 256.1 239.2
17/12/88	4	1.01 E4	1.4 E5	.9999	NBS NBS #4 #4	271.9 264.0 274.7 263.6



18/12/88	4	1.02 E4	7.4 E4	.9976	#4 NBS	258.7 272.6
22/12/88	4	1.09 E4	6.3 E4	.9995	#3	165.1

TABLE 2.8

THE IC RESULTS, USING SODIUM METASILICATE STANDARDS,  
FOR THE CONCENTRATION OF SILICON IN THE NBS OR UNKNOWN #4  
FERROSILICON SAMPLES AND THEIR GRAVIMETRIC COMPARISON

<u>NBS or</u> <u>unknown</u> <u>number</u>	<u>number</u> <u>of anal-</u> <u>ysis</u> <u>per-</u> <u>formed</u>	<u>average</u> <u>[Si]</u> <u>(ppm)</u> <u>by IC</u> <u>method</u>	<u>IC</u> <u>stand-</u> <u>ard de-</u> <u>viation</u> <u>(ppm)</u>	<u>average</u> <u>[Si]</u> <u>(ppm)</u> <u>by</u> <u>gravi-</u> <u>metric</u> <u>method</u>	<u>gravimetric</u> <u>standard</u> <u>deviation</u> <u>(ppm)</u>
NBS	10	257.0	14.3	262.7	.6
unk. #4	12	255.0	12.6	264.3	1.0

**TABLE 2.9**

**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE NBS FERROSILICON SILICON STANDARDS**  
**THAT HAD AND HAD NOT BEEN PRETREATED (30/4/89)**

<u>concentration of silicon in the standard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03 *	3	2.940 E5	8.0 E3
45.04 *	3	4.078 E5	1.1 E4
60.06 *	3	5.534 E5	4.3 E3
blank *	2	2.321 E4	8.6 E3
30.03	3	3.036 E5	2.1 E3
45.04	4	4.437 E5	8.4 E3
60.06	4	5.880 E5	2.0 E4
blank	3	6.007 E4	8.0 E3

Note: an \* indicates the NBS standard was not pretreated

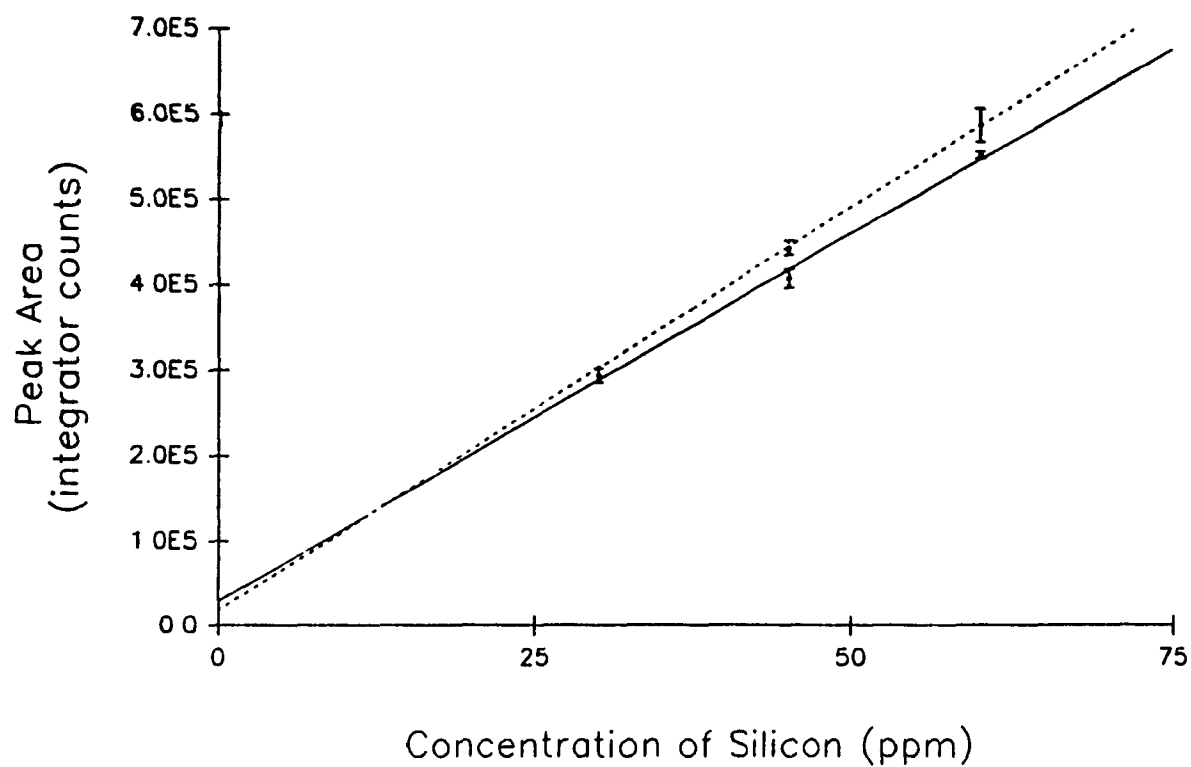


Fig. 2.6 The calibration plot of the silicate peak area versus the concentration of silicon for both the pretreated and untreated NBS ferrosilicon standards (30/4/89).

**TABLE 2.10**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION**  
**AND NUMBER OF INJECTIONS FOR THE PRETREATED**  
**NBS FERROSILICON SILICON STANDARDS AND**  
**UNKNOWN FERROSILICON SAMPLES (24/5/89)**

<u>concentration of</u> <u>silicon in the</u> <u>NBS ferrosilicon</u> <u>standards (ppm)</u> <u>or unknown</u> <u>ferrosilicon</u>	<u>number of</u> <u>inject-</u> <u>ions</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
30.04	4	2.713 E5	1.0 E4
45.06	4	4.110 E5	1.8 E4
60.07	4	5.556 E5	1.3 E4
75.09	4	6.944 E5	1.0 E4
90.11	4	8.204 E5	3.8 E3
120.15	5	1.117 E6	2.7 E4
unk.# 4 (20/250 dilution)	7	5.579 E5	1.5 E4
unk.# 4 (20/250 dilution)	5	5.588 E5	1.5 E4

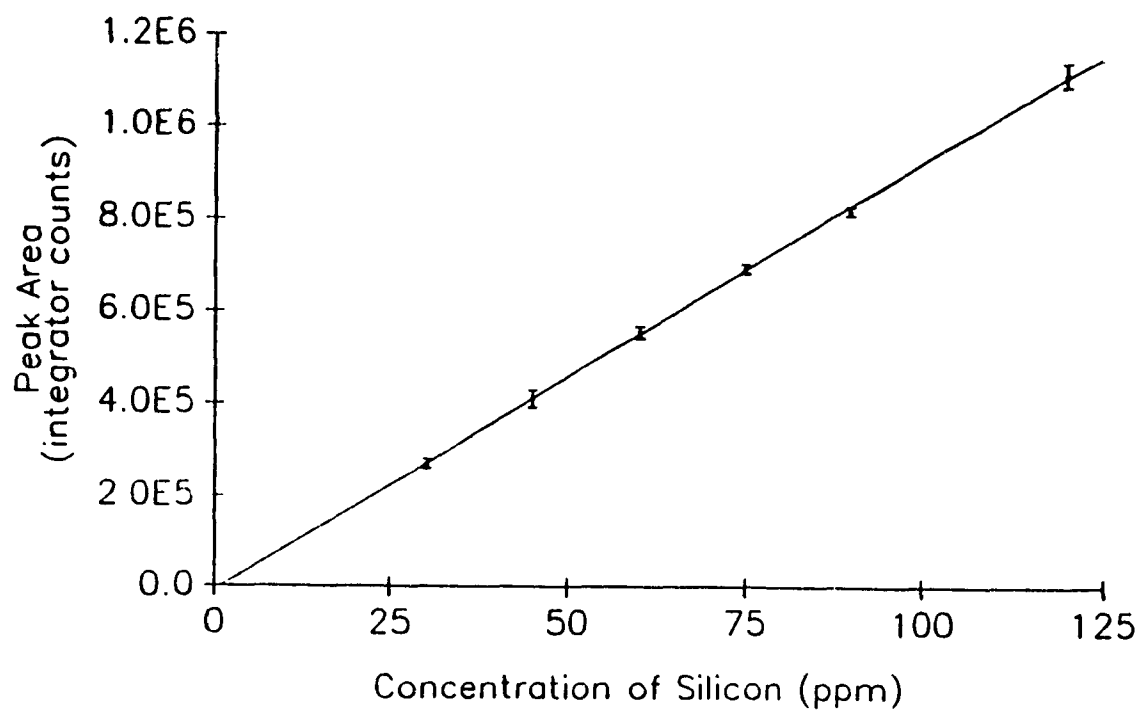


Fig. 2.7 The calibration plot of the silicate peak area versus the concentration of silicon for the pretreated NBS ferrosilicon standards (24/5/89).

**TABLE 2.11**

**THE IC PARAMETERS FOR THE PRETREATED NBS STANDARD**  
**CONCENTRATION OF SILICON VERSUS PEAK AREA AND**  
**THE RESULTS FOR THE UNKNOWN FERROSILICON SAMPLES**

<u>date</u>	<u>num- ber of stand ards</u>	<u>slope</u>	<u>inter- cept</u>	<u>correl ation coeff- icient</u>	<u>un- known ferro- silicon</u>	<u>IC re- sults for [Si] in unknown ferro- silicon (ppm)</u>
22/1/89	4	2.41 E4	2.1 E4	.9998	#3 #5 #5	166.9 187.5 175.0
25/1/89	4	4.10 E4	-2.7 E4	.9993	#3	166.6
29/1/89	3	2.11 E4	2.1 E5	.9861	NONE	NONE
1/2/89	4	1.68 E4	1.4 E4	.9925	#3 #5 #5	179.3 183.0 182.1
11/2/89	4	2.41 E4	-4.6 E4	.9994	#4	262.6
26/2/89	4	2.40 E4	5.6 E4	.9997	#4	265.6
15/3/89	5	2.25 E4	2.4 E5	.9975	#4	759.8
18/3/89	5	2.17 E4	1.4 E4	.9952	#3	466.6
22/3/89	5	1.59 E4	-1.7 E4	.9994	#3 #3 #4	493.3 490.1 250.6
26/3/89	5	2.15 E4	2.4 E4	.9982	#5 #4 #4 #3	500.2 814.5 838.6 470.3

1/4/89	6	9.59 E3	-1.6 E4	.9987	#4 #4 #4 #4	** 590.8 ** 662.1 742.3 745.3
5/4/89	4	8.78 E3	1.0 E5	.9969	#4	** 663.8
7/4/89	7	1.07 E4	-1.1 E4	.9987	NONE	NONE
9/4/89	6	1.11 E4	-5.8 E4	.9974	#4	720.6
18/4/89	7	9.08 E3	-2.3 E4	.9994	#4 #4	** 685.3 744.0
20/4/89	8	9.11 E3	7.8 E3	.9988	#4 #4	** 684.8 712.2
3/5/89	7	9.88 E3	-2.4 E4	.9989	#4 #4	712.3 694.1
8/5/89	7	9.10 E3	-8.9 E3	.9997	#3 #4 #4	425.9 770.4 795.1
24/5/89	6	9.33 E3	-9.0 E3	.9998	#4 #4	759.5 760.7
30/5/89	3	9.79 E3	-3.2 E4	.9980	#4 #4	783.0 782.7
6/6/89	5	1.19 E4	-2.8 E4	.9996	#3 #4	472.2 777.4
20/6/89	4	1.22 E4	-2.5 E4	.9998	#3 #5 #5	477.3 511.8 517.9
21/6/89	4	1.17 E4	-1.9 E4	.9988	#4 #4	732.3 737.2
23/6/89	4	1.18 E4	-1.2 E4	.9995	#3	430.0
5/7/89	4	2.26 E3	-6.8 E3	.9993	#3	467.6
19/7/89	3	2.24 E4	-1.3 E4	.9992	#4 #3	758.6 462.8
29/7/89	4	2.33 E4	-3.5 E2	.9990	#4 #4	266.1 280.7



**\*\* CO<sub>2</sub> formation in pretreatment  
column caused channeling of sample**

**TABLE 2.12**

**THE IC RESULTS FOR THE AVERAGE CONCENTRATION OF SILICON,**  
**USING THE PRETREATED NBS AND UNKNOWN FERROSILICON**  
**SAMPLES AND THEIR GRAVIMETRIC COMPARISON**

<u>un-</u> <u>known</u> <u>number</u>	<u>number</u> <u>of IC</u> <u>analysis</u> <u>per-</u> <u>formed</u>	<u>average</u> <u>% Si</u> <u>using</u> <u>the IC</u> <u>method</u>	<u>IC stan-</u> <u>dard de-</u> <u>viation</u> <u>(% Si)</u>	<u>average</u> <u>% Si</u> <u>using</u> <u>the</u> <u>gravi-</u> <u>metric</u> <u>method</u>	<u>gravi-</u> <u>metric</u> <u>standard</u> <u>deviation</u>
unk. #3	13	47.09	2.32	47.75	.19
unk. #4	25	75.71	3.41	75.51	.29
unk. #5	7	51.55	1.28	51.51	.36

**TABLE 2.13**

**THE RESULTS OF THE CARBON ANALYSIS (PERCENTAGE (%))**  
**PERFORMED ON THE FERROSILICON SAMPLES USING**  
**A LECO INDUCTION FURNACE (10/04/89)**

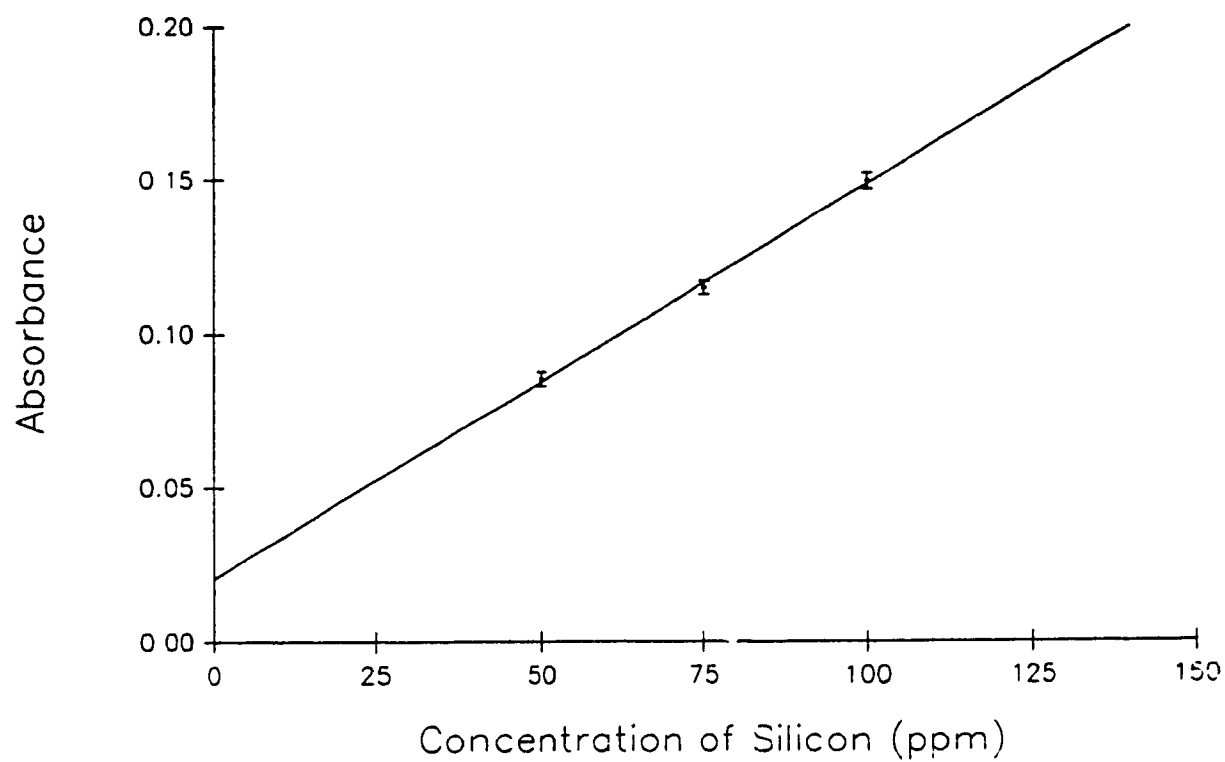
<b><u>ferrosilicon</u></b> <b><u>sample</u></b>	<b><u>percentage carbon (% C)</u></b>
NBS standard	0.044 %
unk. # 1	0.108 %
unk. # 2	0.058 %
unk. # 3	0.058 %
unk. # 4	0.084 %
unk. # 5	0.216 %

**TABLE 2.14**

**ATOMIC ABSORPTION RESULTS TO DETERMINE THE AMOUNT  
OF SILICON IN THE IRON HYDROXIDE PRECIPITATE (8/11/88)**

<u>silicon standard (ppm) or sample</u>	<u>number of readings</u>	<u>average absorbance</u>	<u>standard deviation</u>	<u>percent age silicon</u>
50	4	0.086	.002	---
75	5	0.115	.002	---
100	5	0.150	.003	---
steel standard	4	0.052	.002	0.493
sample 1 (10/25 diliution)	6	0.111	.002	3.53
sample 2	5	0.176	.003	2.42
sample 3 (10/25 di- lution)	6	0.149	.002	5.04

NOTE: Samples 1,2 and 3 were a triplicate (0.5000 g  
ferrosilicon) determination of unk. #4



**Fig. 2.8 The Atomic Absorption calibration plot of absorbance versus concentration of silicon in the iron hydroxide precipitate (8/11/88)**

## **2.4 CRITIQUE OF THE ANALYSIS OF SILICON**

### **IN FERROSILICON USING IC**

The simplest procedure for the analysis of silicon present in a fused (using NaOH) unknown ferrosilicon sample was to compare them to the easily-prepared sodium metasilicate standards ([Si] ppm) using a sodium hydroxide eluent. The choice of the use of sodium hydroxide as the eluent is a logical one because weak acid ions, such as silicate, only exist as anions in a basic solution<sup>2</sup>. Other weak acid anions which require employing a basic eluent, for their effective separation, include borate, cyanide and arsenite<sup>2</sup>.

The results shown in Table 2.6 are an example of the experimental data obtained. It lists the concentration of silicon in the sodium metasilicate standards or the ferrosilicon sample, the number of injections, the average silicate peak area and the standard deviation. The calibration plot of the average peak area (integrator counts) versus the concentration of silicon in the sodium metasilicate standards are shown in Fig. 2.5.

The results obtained, from each of the calibration plots, for the concentration of silicon in the ferrosilicon samples are listed in Table 2.7 by the date the work was performed. This Table also lists the

correlation coefficient, the slope and intercept. The remaining results, in Table 2.7, were obtained using the raw data listed, by the date, in the appendix. The overall average result for the concentration of silicon, in the NBS and unknown #4 ferrosilicon samples, employing the sodium metasilicate standards are listed in Table 2.8. The average results for the concentration of silicon for both the NBS standard and unknown ferrosilicon samples are low compared with their respective gravimetric results. Also, a point of interest is that the standard deviations for the NBS and unknown #4, using the gravimetric methodology, were .18% (or .6 ppm) and .29% (or 1.0 ppm) respectively. These values are much lower than those obtained using the IC technique of 4.1% (or 14.3 ppm) and 3.6% (or 12.6 ppm) respectively. The factors contributing to the low results as well as the larger margin of error, in the IC technique, will be considered later in this section.

A possible explanation for the low results in the original IC methodology, which consisted of comparing the ferrosilicon samples with sodium metasilicate standards, would be the formation of insoluble iron silicates. This may be indicated by the results shown in Table 2.9 and Figure 2.6 which shows that the pretreated NBS standards are have higher peak areas than the unpretreated

standards. This is also indicated by the slopes of these two lines. The pretreated NBS standards had a larger slope ( $9.47 \times 10^3$ ) compared to the untreated ones ( $8.64 \times 10^3$ ). However, this could also be explained by the possibility of suppression of the silicate peak, by overlapping with the pseudo peak, in the untreated ferrosilicon samples. This could have reduced the electrical signal of the silicate peak, since they have opposite polarities, in the case of the untreated ferrosilicon samples. Thus, more work would be required to differentiate between these two cases.

Another possible explanation for the low results, in the untreated ferrosilicon samples, would be the loss of insoluble silicates during the filtering and rinsing steps. Any insoluble silicates could get trapped in the iron hydroxide precipitate during the filtering step, just after removal of the samples from the pressure cooker. This was supported by the atomic absorption results. The results, for the amount of silicon remaining in the iron hydroxide precipitate, shown in Table 2.14 indicate that the loss of silicates was a random occurrence because they vary to such a large degree.

The separation of the silicate peak from the pseudo peak was a difficult obstacle, in the case of the unknown and NBS ferrosilicon samples. Their fusion with sodium



hydroxide in a 10:1 flux to sample ratio provided the ferrosilicon samples with a large number of unwanted sodium and hydroxide ions that eluted off the separator column in the dead volume. Also as mentioned in section 2.1.4, upon injection onto the separator column the eluent hydroxide anions were displaced from the positively-charged sites, on the resin, by the solute silicate anions in the previously-fused ferrosilicon samples. Also all the sodium ions present in the sample, as  $\text{Na}_2\text{SiO}_3$  (or  $\text{Na}_4\text{SiO}_4$ ) passed through the anion separator column unretained. Therefore, the pseudo peak was extremely large and often eluted out for 3.0-4.0 minutes at the beginning of each injection. The pseudo peak interfered with the later eluting silicate anion (retention time 6-7 minutes). This is shown in Fig 2.9. Because of this interference, it was difficult to obtain reproducible peak areas from injection to injection for the ferrosilicon samples. On many occasions resolution of these peaks could not be obtained at all.

In the case of the sodium metasilicate silicon standard solutions the pseudo peak present, however, was much smaller in these unfused standards. The duration of the pseudo peak was approximately 1.5 minutes. This is

shown in Fig. 2.10. In most instances resolution of the pseudo peak from the silicate peak was easily obtained with the IC conditions employed.

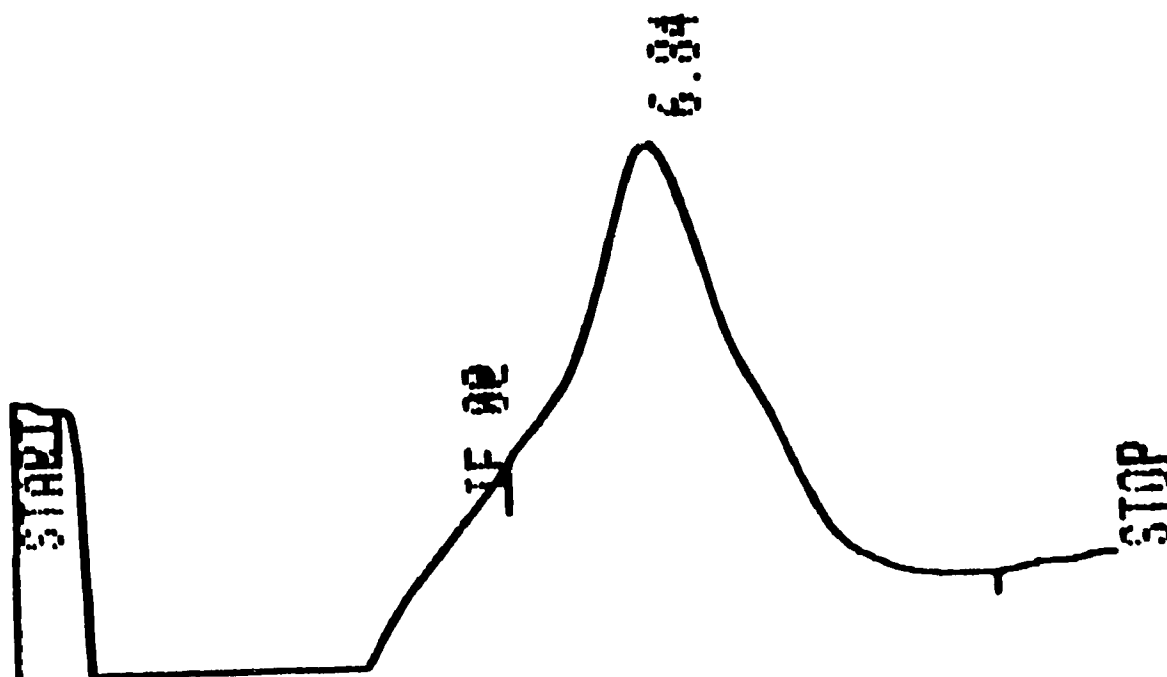


Fig. 2.9 The overlapping of the pseudo and silicate peaks in the ferrosilicon samples. This is illustrated by a 10/25 dilution of the NBS (.35g/1L) sample employing a flow rate of 2.5 ml/min. and a 2mM NaOH eluent concentration.

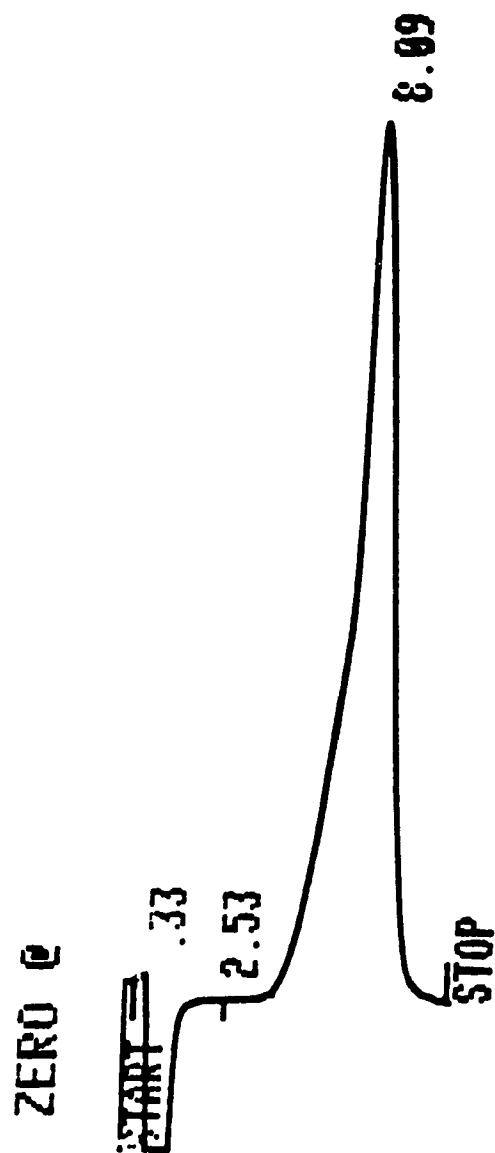


Fig. 2.10 A chromatogram showing that the pseudo peak is resolved from the silicate peak in the sodium metasilicate standards. This illustration had a silicon concentration of 250 ppm and was obtained employing a flow rate of 2.0 ml/min using a 3mM NaOH concentration.

The problem of resolving the silicate peak from the pseudo peak in the ferrosilicon samples was approached by a few logical alternative methodologies. The first approach involved a simple dilution (10/25) of the original ferrosilicon sample. The second involved the use of a smaller injection volume (i.e. less than 100  $\mu$ l). Both of these cases, under proper IC parameters allowed for the partial resolution of the peaks. However, in both of these instances the conductance due to both the pseudo peak and silicate peaks were reduced accordingly. Thus, the electrical signal (4-10  $\mu$ S) observed as the silicate peak ( $\Delta$ G) was small compared with a baseline having a large background conductivity (600  $\mu$ S for 3mM NaOH). Hence, the signal to noise ratio (S/N) was decreased substantially with the dilution or smaller injection volume causing more variation in the results. So, although this method allowed for the quantitation of silicon in the fused ferrosilicon samples it was still undesirable because of the decrease in the S/N ratio.

When the concentration of the sodium hydroxide eluent was lowered to around 0.8-1.2 mM the background conductance was also lowered accordingly (approx. 200-250  $\mu$ S). The weaker eluent aided the resolution of the pseudo and silicate peaks. However, the retention time of the silicate peak was longer, in the range of ten minutes,

when using the weaker sodium hydroxide eluent. Most of the results for the ferrosilicon samples, mentioned earlier, were obtained using both dilutions of the samples and a weak sodium hydroxide eluent. A consequence of the use of the weaker NaOH eluent was fronting of the silicate peak. An example of this is shown in Fig. 2.11.

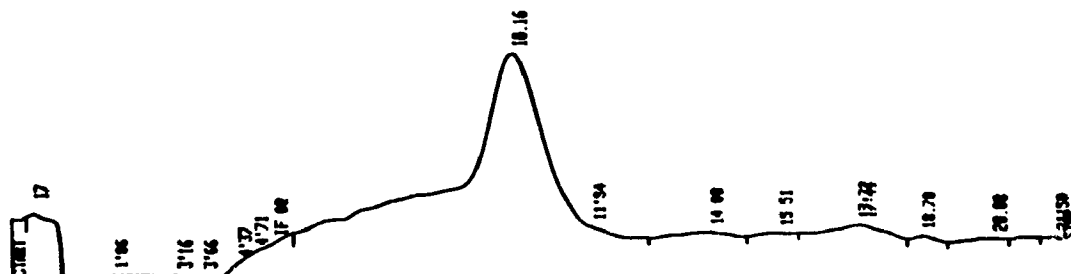


Fig. 2.11 The partial resolution of the silicate from the pseudo peak and the fronting that occurred. The illustration used is a 10/25 dilution of unknown ferrosilicon # 3 using a 1.2 mM NaOH eluent at a flow rate of 2.0 ml/min.

In the case of the ferrosilicon samples a later eluting peak was also found and identified as carbonate, by spiking a sample with sodium carbonate. This peak

eluted at approximately 18-22 minutes, causing the time of obtaining the chromatogram to be greatly increased, when employing the weaker concentrations of NaOH eluent. This is shown in Fig. 2.11 where the small peak at 17 1/2 minutes is due to carbonate. This author believes that there are two possible origins for the carbonate peak:

- (1) carbon present in the starting ferrosilicon sample;
- (2) the absorption of carbon dioxide gas, present in the atmosphere, by the sodium hydroxide flux.

Fritz, Gjerde and Polhandt<sup>2</sup> state that hydroxide is an effective eluent for easily eluting monovalent anions such as fluoride, chloride, nitrate and cyanide. However, it is less effective in eluting multivalent anions such as carbonate and sulfate since they elute off very slowly.

The problem of resolving the silicate peak from the pseudo peak and still obtaining a reasonable S/N ratio was also approached by changing the eluent from sodium hydroxide to one having a lower background conductance (i.e. less mobile). However, different concentrations of benzoic acid and potassium hydrogen phthalate (KHP) were found to be ineffective as eluents although they provided an attractive lower background conductance (100-200  $\mu$ S). These eluents were ineffective because for all practical purposes the silicate anion was bound irreversibly

(retention time of more than 30 minutes at best) to the positively-charged sites on the resin. This is shown in Fig. 2.12, where the silicate peak has not eluted off the column even after 30 minutes using a 2.2 mM KHP eluent.

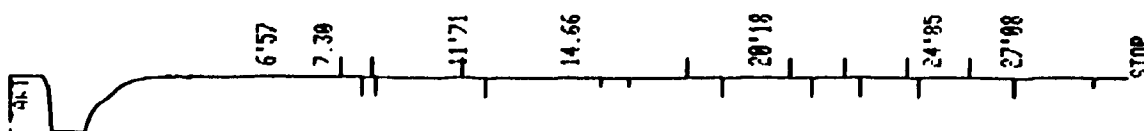


Fig. 2.12 The ineffective elution of the silicate peak using a 2.2 mM KHP eluent (baseline conductance of 216  $\mu S$ ) and flow rate of 3.5 ml/min..

An attempt at reducing the background conductance by using mixtures of sodium hydroxide and sodium benzoate was also tried. However, another extra peak occurred when this mixture was used, often interfering with the silicate peak. This is shown in Fig. 2.13. The first peak, after the pseudo peak, was identified by spiking a sample with sodium metasilicate as the silicate peak. In



this instance the silicate peak not only had to be resolved from the positive pseudo peak that eluted out prior to it but also from the extra negative peak that eluted out after it. Thus, this eluent mixture was again found to be ineffective in providing the required resolution for the quantitation of the silicate peak. In fact, a similar observation was made by Fritz, Gjerde and Pohlhandt<sup>2</sup>. They stated that "attempts to use a basic solution of benzoate or phthalate as the eluent have given extra positive and negative peaks". They have proposed that the extra peaks originate from the fact that the eluent is actually a mixture of anions (either a mixture of hydroxide and benzoate or hydroxide and phthalate).

Another alternative eluent was KOH, which has also been used in the IC determination of silicates<sup>1,24</sup> in a water matrix. However, the KOH eluents employed in this work produced a large positive peak just after the silicate peak, interfering with it. This is shown in Fig. 2.14. Also a KOH eluent would have a higher background conductance than a NaOH eluent because the potassium ion has a higher equivalent conductance than the sodium ion<sup>2</sup>. This, of course, would increase the background conductance and decrease the S/N ratio, which is undesirable.

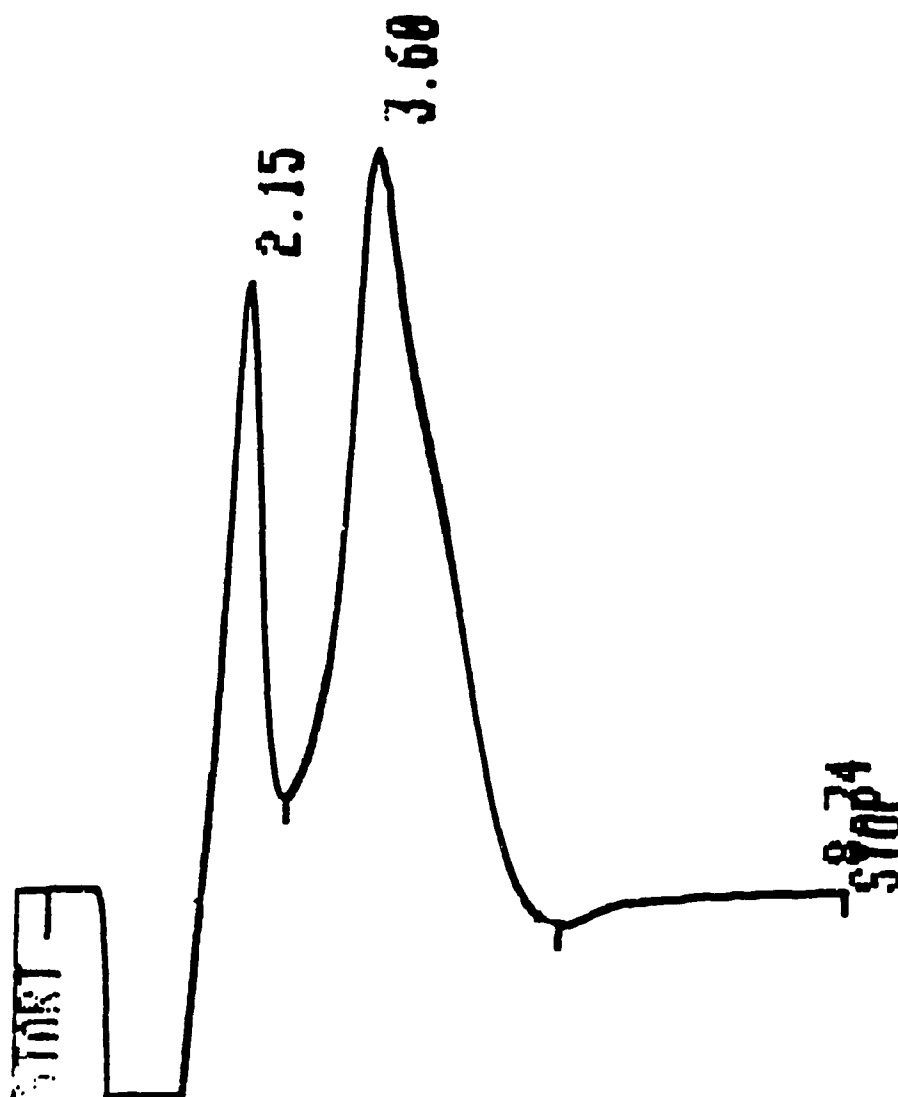


Fig. 2.13 The difficulty in resolving the silicate peak from both the pseudo and "second negative" peak in the chromatogram using a sodium hydroxide (3mM) and sodium benzoate (1mM) mixture as the eluent. This is illustrated by a 138 ppm NBS ferrosilicon sample using a flow rate of 2.0 ml/min..

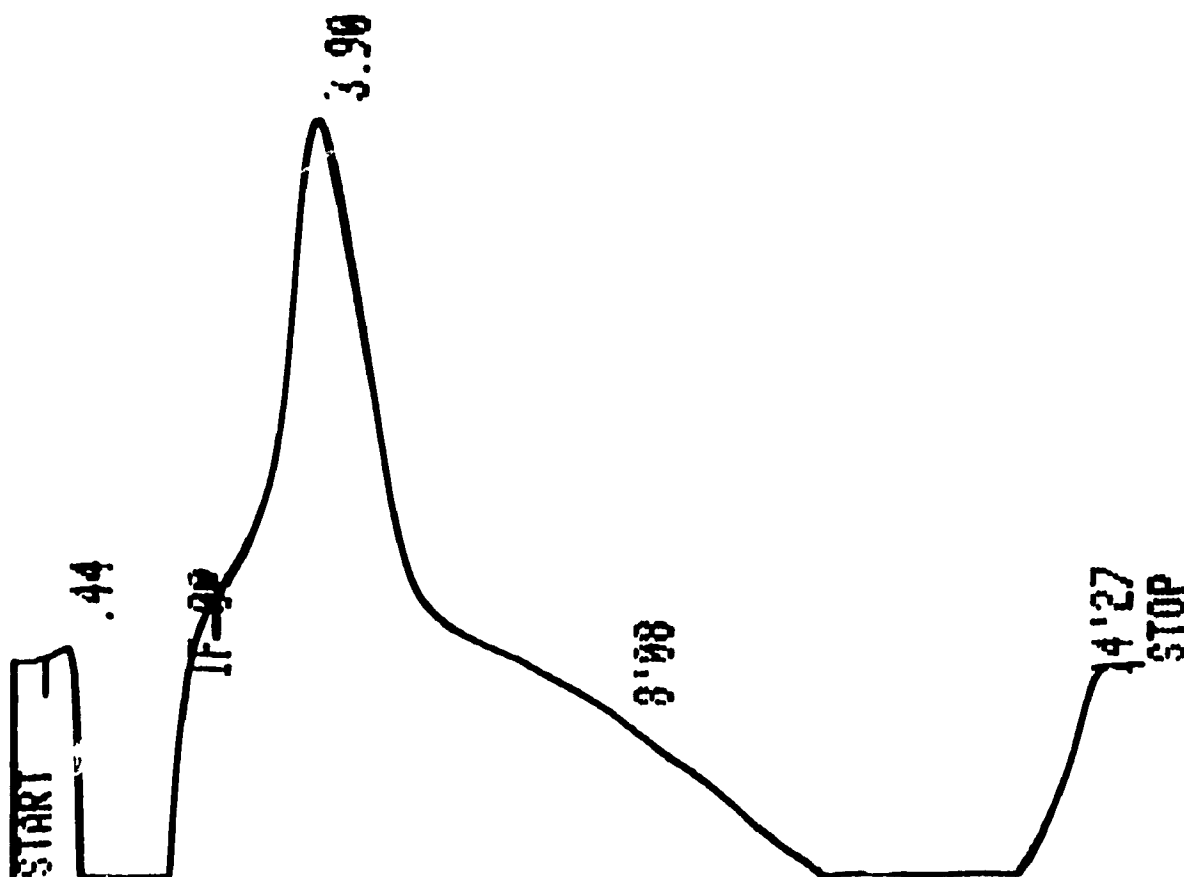


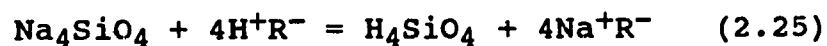
Fig. 2.14 The extra positive peak present when using a KOH eluent. This is illustrated by a 50% dilution of the NBS ferrosilicon sample (.35g/1L). The eluent concentration was 3mM and the flow rate was 2.5 ml/min. (baseline conductance of 718  $\mu$ s).

Another approach to the problem of resolving the silicate peak from the large pseudo peak present in the ferrosilicon samples would involve the use of another column. However, the Hamilton PRP-X100, used in this work was chosen because of its proven ability to separate silicates and other weak acid anions<sup>22</sup>. Thus, changing the column was an expensive and illogical choice.

The resolution could have been obtained by increasing the length of the separator column. This could be done by simply obtaining a longer separator column or by placing two separator columns in series. Since, the Hamilton PRP-X100 separator column, was the longest available (25 cm) on the market at this time, this eliminated the former choice. The other alternative method would have been to use two columns in series to increase the separating capacity. However, placing two columns in series would have had drawbacks including peak broadening, an increased retention time for all the peaks in the chromatogram and a higher pump pressure to provide the same eluent flow rate. This would not be the best choice available for the health of the older Waters instrument, thus, it was avoided.

The problem of resolving the silicate from the pseudo peak was solved by simply reducing its size so it no longer interfered with the silicate peak. The

pretreatment, introduced earlier, decreased the amount of cations in the injected sample (i.e. fused ferrosilicon and remaining flux) by simply eluting both the NBS standard and unknown ferrosilicon samples through a cation-exchange resin in its protonated form. This left the silicic acid in a background of water:



The pretreatment reduced the previously large positive pseudo peak substantially, if not totally, leaving only a smaller negative peak which was easily resolved from the silicate peak. This is shown in Fig. 2.15.

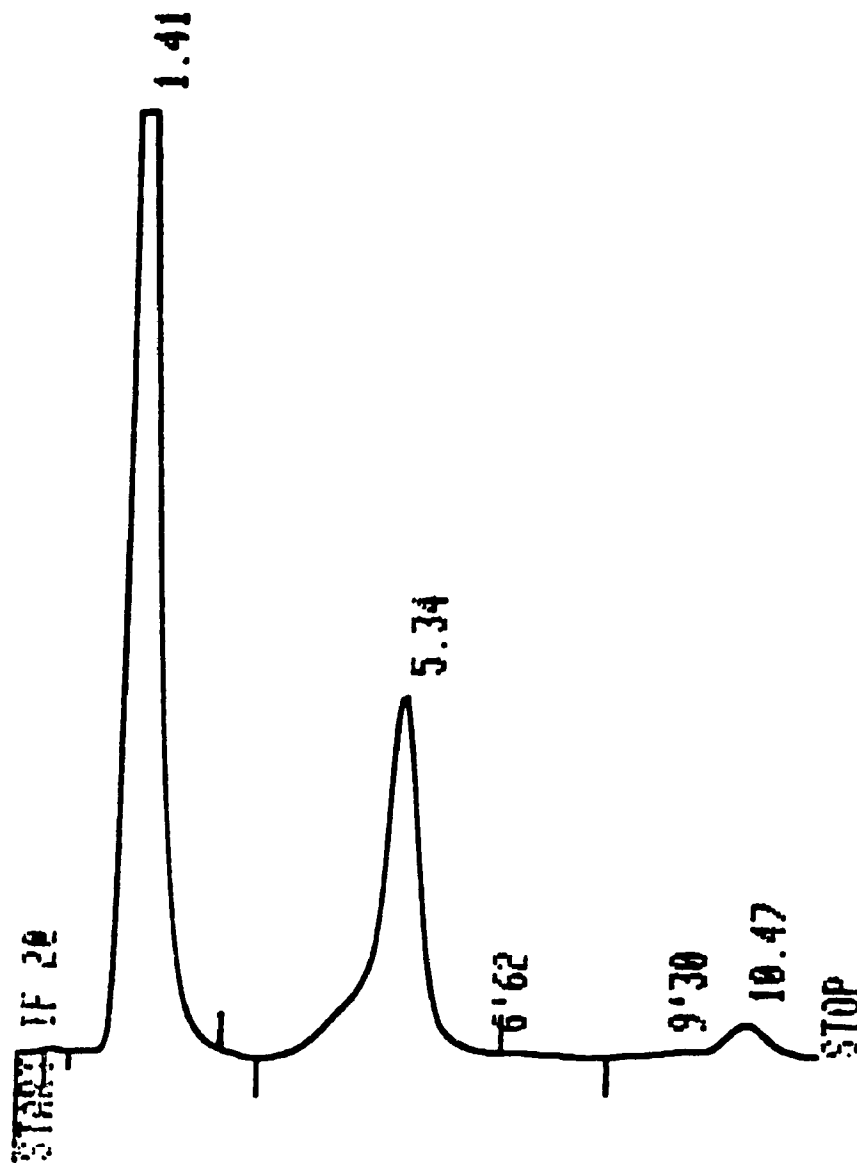


Fig. 2.15 The reduction of the pseudo peak after pretreatment allowing the resolution of the silicate peak from the smaller negative hydroxide peak. This is illustrated by a 45.06 ppm NBS standard using a 2.5 mM NaOH eluent (baseline 537  $\mu$ s).

Employing the pretreatment allowed for the use of higher silicon concentration ferrosilicon standards. That is, a larger initial ferrosilicon sample and flux could be fused together providing a larger conductance signal (i.e.  $\Delta G$ ) for the silicate peak. This allowed both a larger range (up to 210 ppm) for the calibration plot of the NBS ferrosilicon samples and a larger conductance signal for the unknown ferrosilicon samples while still providing the required resolution and a somewhat better S/N ratio. The larger range would be required if this technique was used on an industrial scale so that all the different foundry and steel making grades, shown in Tables 1.1 and 1.2, could be analysed easily.

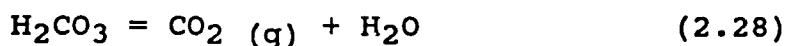
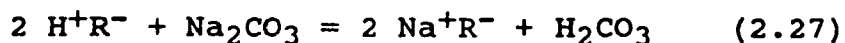
A sample of the results obtained using the pretreated ferrosilicon methodology are shown in Table 2.10. It lists the concentration of the NBS standard or the unknown ferrosilicon sample, the number of 100  $\mu$ l injections made, the average silicate peak area and the standard deviation. The calibration plot, for this example, of the average concentration of silicon versus the silicate peak area is shown in Fig. 2.7. The error bars shown, for each point, are simply the standard deviation for that particular NBS standard.

The final results obtained, from each calibration plot, for the concentration of silicon in the unknown ferrosilicon samples are listed in Table 2.11 by the date the work was performed. This Table also lists the linear regression correlation coefficient, and the slope and intercept for the line in question. The remaining results, in Table 2.11, were obtained using the raw data listed, by the date, in the appendix. The overall average results for the percentage of silicon in the unknown ferrosilicon samples are shown in Table 2.12. The results for the percentage silicon indicate that the IC methodology can provide reasonable accuracy compared to the gravimetric methodology. However, the standard deviations for the IC methodology compared with those of the gravimetric methodology indicate that the gravimetric methodology is much more precise. This could be attributed to the problem of reading a small change in conductance, as the silicate peak, on the large baseline provided by the high background conductance of the sodium hydroxide eluent in the IC methodology.

A problem that was encountered, when the pretreatment was employed, was the formation of carbon dioxide gas as the unknown samples were eluted through the high capacity cation-exchange resin. The gas caused the resin to lift, allowing the channeling of the silicate sample



through the resin. This caused losses of the silicates in the cation-exchange column. The two samples, that this occurred frequently with, were unknown ferrosilicon samples # 4 and 5. Table 2.13 shows that these two samples, out of the three analysed, had larger contents of carbon inherent to them. It is possible that sodium carbonate was formed during the fusion, from the carbon inherent to the ferrosilicon samples, or it may have been adsorbed by the remaining sodium hydroxide flux. In any case, when the sodium carbonate was placed on the cation-exchange resin in its proton form, it was converted to carbonic acid, which due to its instability decomposed to carbon dioxide gas and water.



Prior to the SCIC determination of anions, large amounts of metal ions present in the sample could cause interferences, therefore, they should be removed. The interfering metals can be divided into two classes: (1) The first class includes large quantities of metal anions that may overload the separator column; (2) The second class includes metals that will precipitate as hydroxides in an alkaline eluent<sup>2</sup>. This results in a pressure

buildup in the system and deterioration of the separator column. In this work both types of these interferences were encountered.

The first class was encountered with the formation of the permanganate ion, during the fusion, from the manganese inherently present in some of the ferrosilicon samples available to this author. Solutions from unknowns # 1,2 and 6 had the characteristic purple permanganate colour and a deposit of brown manganese dioxide. In fact the samples contained 46%, 62% and 68% manganese respectively. Because of the extremely large manganese content these samples were not "true" ferrosilicon samples but ferrosilicomanganese samples. Upon injection of any of these samples onto the PRP-X100 separator column, the large amount of the permanganate anion present "overloaded" it. Therefore, results could not be obtained for these unknown samples.

The second class was encountered with the formation and precipitation of iron hydroxide in the highly alkaline environment provided by the sodium hydroxide eluent. In fact, this was also observed in the original 1L volumetric flask, where upon sitting around, the iron hydroxide would form and settle on the bottom of the flask. After a few injections of the unpretreated ferrosilicon samples, the iron hydroxide would build up

in the precolumn and possibly the separator column, blocking them and causing an increase in the pressure required to provide the same eluent flow rate. This problem was resolved by disconnecting the precolumn from the separator column and detector, reversing it and washing it with the eluent for half an hour. The separator column was reconnected, the precolumn disconnected, and the eluent was again pumped through it to remove any particles blocking it.

A major problem encountered with the IC method, employing a sodium hydroxide eluent, was the rapid deterioration of the pump seals. This caused the seals to leak and required them to be changed frequently. This resulted in the unexpected and expensive replacement of the seals (approx. \$ 80 per pair).

### 3 CONCLUSION:

This study examined the possibility of replacing the accepted gravimetric methodology with a SCIC methodology for the analysis of silicon in ferrosilicon. The basic objective of the study was to develop an SCIC methodology that was: (1) faster than the gravimetric methodology; (2) more precise or reproducible than the gravimetric methodology. However, this author found that the SCIC methodology, combined with its required pretreatment of the ferrosilicon samples to decrease the pseudo peak, was in fact slower than the gravimetric methodology. It was also found that the SCIC methodology, employed in this work, was less reproducible than its gravimetric counterpart. It was less reproducible because of a poor signal to noise ratio (S/N). This occurred because of the inherent problem of reading a small conductance signal ( $\Delta G$ ), observed as the silicate peak, on the large baseline (background conductance) provided by the sodium hydroxide eluent. Of course, a poor S/N ratio is extremely undesirable in any analysis. Hence, the replacement of the gravimetric methodology with the SCIC methodology, developed in this work, is unlikely.

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**APPENDIX:****PRESENTATION OF SCIC RAW DATA**

**TABLE 2.15**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE SODIUM METASILICATE SILICON**  
**STANDARDS AND FERROSILICON SAMPLE UNKNOWN # 4 (19/11/88)**

<u>concentra-</u> <u>tion of</u> <u>metasilicate</u> <u>silicon</u> <u>standard</u> <u>(ppm) or un-</u> <u>known</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integrator</u> <u>counts)</u>	<u>standard</u> <u>deviation</u>
50	3	5.614 E5	6.0 E3
100	5	1.095 E6	4.7 E4
150	5	1.556 E6	3.7 E4
200	3	1.977 E6	4.1 E4
250	6	2.542 E6	1.3 E5
unk. # 4	4	2.614 E6	2.1 E5



**TABLE 2.16**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE SODIUM METASILICATE SILICON**  
**STANDARDS AND FERROSILICON SAMPLE UNKNOWN # 4 (21/11/88)**

<u>concentra-</u> <u>tion of the</u> <u>metasilicate</u> <u>silicon</u> <u>standard</u> <u>(ppm) or un-</u> <u>known</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integrator</u> <u>counts)</u>	<u>standard</u> <u>deviation</u>
100	2	1.134 E6	3.0 E4
150	5	1.663 E6	9.0 E4
200	4	2.127 E6	2.8 E3
250	6	2.813 E6	7.9 E4
unk. # 4	4	3.031 E6	4.5 E5

**TABLE 2.17**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE SODIUM METASILICATE**  
**SILICON STANDARDS (24/11/88)**

<u>concentration</u> <u>of metasili-</u> <u>cate silicon</u> <u>standard</u> <u>(ppm)</u>	<u>number of</u> <u>injec-</u> <u>tions</u>	<u>average peak area</u> <u>(integrator</u> <u>counts)</u>	<u>standard</u> <u>deviation</u>
100	3	1.139 E6	1.2 E4
150	4	1.607 E6	5.3 E4
200	3	2.104 E6	1.1 E5
250	6	2.600 E6	5.4 E4

**TABLE 2.18**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION**  
**AND NUMBER OF INJECTIONS FOR THE SODIUM METASILICATE**  
**SILICON STANDARDS AND UNKNOWN FERROSILICON SAMPLES**  
**(25/11/88)**

<u>concentration of silicon in the metasilicate stan- dards (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
50	3	5.917 E5	1.1 E4
150	2	1.522 E6	2.4 E4
250	6	2.530 E6	5.6 E4
unk. # 4	5	2.553 E6	1.3 E4

**TABLE 2.19**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION**  
**AND NUMBER OF INJECTIONS FOR THE SODIUM**  
**METASILICATE SILICON STANDARDS (1/12/88)**

<u>concentration of silicon in the metasilicate stan- dards (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
50	4	5.549 E5	2.3 E4
100	9	1.111 E6	7.4 E4
150	5	1.489 E6	3.5 E4
200	5	2.557 E6	4.3 E4

**TABLE 2.20**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE METASILICATE SILICON STANDARDS**  
**AND UNKNOWN FERROSILICON SAMPLES (2/12/88)**

<u>concentration of silicon in the metasilicate stan- dards (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
150	3	1.736 E6	3.2 E4
200	3	2.290 E6	2.7 E4
250	3	2.846 E6	2.9 E4
unk. # 4	9	2.964 E6	2.7 E4
unk. # 4	5	2.819 E6	2.2 E4

**TABLE 2.21**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION**  
**AND NUMBER OF INJECTIONS FOR THE SODIUM**  
**METASILICATE SILICON STANDARDS AND A 40%**  
**DILUTION OF THE NBS STANDARD (9/12/88)**

<u>concentration of</u> <u>silicon</u> <u>in the metasilicate standard or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integrator counts)</u>	<u>standard</u> <u>deviation</u>
50	4	6.097 E5	5.7 E4
100	7	1.130 E6	5.2 E4
150	12	1.651 E6	9.5 E4
250	7	2.735 E6	9.9 E4
NBS (10/25 dilution) sample 1	11	1.182 E6	1.0 E5
NBS (10/25 dilution) sample 2	9	1.244 E6	1.5 E5

**TABLE 2.22**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION**  
**AND NUMBER OF INJECTIONS FOR THE SODIUM**  
**METASILICATE SILICON STANDARDS AND THE**  
**NBS AND UNKNOWN FERROSILICON SAMPLE (11/12/88)**

<u>concentration of the silicon in the metasilicate stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
100	10	1.139 E6	8.3 E4
150	4	1.728 E6	5.4 E4
250	4	2.725 E6	4.3 E4
NBS (10/25 dilu- tion)	6	1.138 E6	5.9 E4
NBS (10/25.3 dilu- tion)	6	1.147 E6	7.9 E4
unk. # 4 (10/25 dilution)	5	1.156 E6	7.3 E4

**TABLE 2.23**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE SODIUM METASILICATE**  
**SILICON STANDARDS AND THE NBS FERROSILICON SAMPLE (15/12/88)**

<u>concentration of silicon in the metasilicate stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
100	4	1.093 E6	6.6 E4
150	4	1.604 E6	4.1 E4
250	4	2.688 E6	8.3 E4
NBS	3	2.570 E6	2.3 E4
NBS (10/25 dilu- tion)	5	1.110 E6	6.0 E4
NBS (10/25 dilu- tion)	4	1.038 E6	5.1 E4



**TABLE 2.24**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE SODIUM METASILICATE SILICON STANDARDS**  
**AND THE NBS AND UNKNOWN FERROSILICON SAMPLES (17/12/88)**

<u>concentration of</u> <u>silicon in the</u> <u>metasilicate stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
100	12	1.166 E6	6.9 E4
150	3	1.657 E6	1.7 E4
200	4	2.167 E6	4.2 E4
250	9	2.687 E6	7.9 E4
NBS (10/25 dilu- tion)	5	1.247 E6	6.1 E4
NBS (10/25 dilu- tion)	4	1.215 E6	3.5 E4
unk.# 4 (7/10 dilution)	3	2.095 E6	9.5 E4
unk.# 4	2	2.819 E6	8.5 E4

**TABLE 2.25**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE SODIUM METASILICATE SILICON STANDARDS**  
**AND THE NBS AND UNKNOWN FERROSILICON SAMPLES (18/12/88)**

<u>concentration of silicon in the metasilicate stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
50	2	5.751 E5	2.6 E4
100	5	1.167 E6	4.9 E4
150	4	1.524 E6	2.2 E4
250	6	2.602 E6	9.1 4
NBS (10/25 dilu- tion)	5	1.18 E6	6.2 E4
unk. # 4 (10/25 dilution)	3	1.13 E6	4.5 E4

**TABLE 2.26**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE SODIUM METASILICATE SILICON STANDARDS**  
**AND THE NBS AND UNKNOWN FERROSILICON SAMPLES (22/12/88)**

<u>concentration of</u> <u>silicon in the</u> <u>metasilicate stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
50	3	6.089 E5	3.7 E4
100	5	1.128 E6	4.4 E4
150	5	1.745 E6	5.4 E4
250	4	2.781 E6	3.3 E4
unk. # 3	3	1.867 E6	2.7 E4

**TABLE 2.27**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (22/1/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
25.80	5	6.375 E5	5.2 E3
52.55	3	1.288 E6	2.6 E4
65.70	3	1.619 E6	4.0 E3
78.80	2	1.906 E6	7.6 E4
unk.# 3 (1/10 diliution)	6	4.228 E5	6.4 E3
unk.# 5 (1/10 dilution)	4	4.724 E5	1.1 E4
unk.# 5 (1/10 dilution)	3	4.421 E5	6.4 E3

**TABLE 2.28**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (25/1/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon sili-</u> <u>con standard (ppm)</u> <u>or unknown fer-</u> <u>rosilicon</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
26.27	3	1.067 E6	5.9 E4
52.55	4	2.078 E6	8.1 E4
65.70	5	2.697 E6	1.8 E5
78.51	3	3.193 E6	3.8 E4
unk. # 3 (1/10 dilution)	6	6.560 E5	7.0 E4

**TABLE 2.29**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON**  
**SILICON STANDARDS AND UNKNOWN FERROSILICON (29/1/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown ferro- silicon</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
52.55	2	1.209 E6	2.6 E4
105.10	4	2.640 E6	5.7 E4
157.65	3	3.424 E6	3.5 E4
unk.# 3 (50/100 dilution)	3	1.274 E6	3.7 E4
unk.# 5 (50/100 dilution)	2	1.667 E6	1.6 E4
unk.# 5 (50/100 dilution)	2	1.729 E6	9.6 E3

**TABLE 2.30**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLE (1/2/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
52.6	4	1.008 E6	7.4 E3
105.1	5	1.990 E6	2.5 E4
157.7	5	2.630 E6	6.0 E4
183.9	5	3.334 E6	7.3 E4
unk. # 3 (10/25 dilution)	4	1.346 E6	4.0 E3
unk. # 5 (10/25 dilution)	5	1.371 E6	3.8 E4
unk. # 5 (10/25 dilution)	4	1.365 E6	2.5 E4

**TABLE 2.31**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLE (11/2/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
30.03	3	6.827 E5	1.4 E4
60.06	4	1.431 E6	9.1 E3
120.12	3	2.766 E6	5.2 E4
180.17	6	4.329 E6	4.7 E4
unk. # 4 (40/250 dilution)	8	9.651 E5	2.8 E4



**TABLE 2.32**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLE (26/2/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
30.03	4	7.626 E5	2.3 E4
60.06	6	1.502 E6	2.8 E4
180.17	5	4.442 E6	5.2 E4
210.20	8	5.048 E6	7.7 E4
unk. # 4	5	1.076 E6	1.6 E4

**TABLE 2.33**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (15/3/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
60.06	4	1.510 E6	3.4 E4
90.08	7	2.260 E6	5.0 E4
120.11	4	3.042 E6	2.0 E4
180.17	5	4.386 E6	5.0 E4
210.20	4	4.848 E6	8.5 E4
unk. #4 (30/250 dilution)	11	2.288 E6	5.6 E4

**TABLE 2.34**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (18/3/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
60.06	4	1.371 E6	3.4 E4
90.08	4	2.042 E6	6.1 E4
120.11	3	2.867 E6	6.3 E4
180.17	4	4.195 E6	5.0 E4
210.20	3	4.535 E6	6.1 E4
unk. # 3 (40/250 dilution)	5	1.755 E6	4.1 E4

**TABLE 2.35**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS SILICON STANDARDS**  
**AND UNKNOWN FERROSILICON SAMPLES (22/3/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dards (ppm) or unknown ferrosili- con samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03	3	4.392 E5	5.9 E3
60.06	4	9.252 E5	1.2 E4
90.08	3	1.426 E6	1.5 E4
120.11	3	1.933 E6	2.0 E4
180.17	4	2.807 E6	2.6 E4
unk. #3 (40/250 dilution)	5	1.234 E6	1.0 E4
unk. #3 (40/250 dilution)	5	1.226 E6	1.3 E4
unk. #4 (40/250 dilution)	6	1.572 E6	1.4 E4

**TABLE 2.36**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (26/3/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
60.06	3	1.449 E6	2.7 E4
90.08	5	2.174 E6	1.8 E4
120.11	4	2.939 E6	4.9 E4
180.17	4	4.140 E6	5.7 E4
210.20	3	4.687 E6	4.6 E4
unk.# 3 (40/250 dilution)	3	1.854 E6	1.7 E4
unk.# 4 (30/250 dilution)	5	2.338 E6	1.9 E4
unk.# 4 (40/250 dilution)	4	3.122 E6	9.7 E4
unk.# 5 (40/250 dilution)	4	1.957 E6	4.9 E4

**TABLE 2.37**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON (1/4/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03	3	2.594 E5	4.4 E3
60.06	7	5.657 E5	9.1 E3
90.08	7	8.709 E5	1.9 E4
120.11	7	1.117 E6	1.1 E4
unk.# 4 (40/250 dilution)	8	8.897 E5	3.5 E4
unk.# 4 (20/250 dilution)	5	4.914 E5	2.2 E4
unk.# 4 (20/250 dilution)	8	5.529 E5	1.8 E4
unk.# 4 (20/250 dilution)	6	5.552 E5	8.9 E3

**TABLE 2.38**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON**  
**SILICON STANDARDS AND UNKNOWN FERROSILICON (5/4/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
60.06	3	6.192 E5	7.0 E3
75.07	4	7.620 E5	1.4 E4
90.08	4	9.081 E5	8.0 E3
105.10	4	1.010 E6	2.2 E4
unk.# 4 (20/250 dilution)	2	5.660 E5	1.9 E3

**TABLE 2.39**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON**  
**SILICON STANDARDS AND THE BLANK (7/4/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
30.03	3	3.063 E5	1.8 E4
45.04	5	4.789 E5	4.2 E3
60.06	4	6.454 E5	6.5 E3
75.07	3	7.695 E5	1.6 E4
90.08	4	9.663 E5	1.3 E4
105.10	4	1.088 E6	4.7 E4
120.11	4	1.292 E6	2.2 E4
blank	4	9.455 E4	1.4 E4



**TABLE 2.40**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON (9/4/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>ferrosilicon stan-</u> <u>dard (ppm) or</u> <u>unknown</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
45.04	5	4.733 E5	2.0 E4
60.06	8	5.749 E5	2.4 E4
75.07	8	7.590 E5	2.1 E4
90.08	4	9.503 E5	9.5 E3
105.10	4	1.102 E6	1.4 E4
120.11	4	1.283 E6	2.4 E4
unk.# 4 (20/250 dilution)	4	5.749 E5	1.7 E4

**TABLE 2.41**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON**  
**SILICON STANDARDS AND UNKNOWN FERROSILICON (18/4/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03	4	2.718 E5	3.6 E3
45.04	5	4.209 E5	8.9 E3
60.06	4	5.747 E5	8.3 E3
75.07	4	6.942 E5	4.8 E3
90.08	5	8.657 E5	6.5 E3
105.10	5	9.963 E5	1.9 E4
120.11	4	1.165 E6	2.2 E4
unk.# 4 (20/250 dilution)	4	5.142 E5	5.1 E3
unk.# 4 (20/250 dilution)	4	5.602 E5	4.8 E3
blank	4	3.771 E4	1.3 E4

**TABLE 2.42**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND**  
**NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON**  
**SILICON STANDARDS AND UNKNOWN FERROSILICON (20/4/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03	5	2.644 E5	9.2 E3
45.04	4	4.032 E5	9.9 E3
60.06	5	5.595 E5	7.2 E3
75.07	6	6.898 E5	1.6 E4
90.08	5	8.427 E5	1.1 E4
105.10	6	9.701 E5	1.1 E4
120.11	5	1.141 E6	1.5 E4
180.17	3	1.617 E6	9.6 E3
unk.# 4 (20/250 dilution)	3	5.066 E5	6.2 E3
unk.# 4 (20/250 dilution)	4	5.266 E5	1.6 E3

**TABLE 2.43**

**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON STANDARDS AND UNKNOWN FERROSILICON (3/5/89)**

<u>concentration of silicon in the NBS ferrosilicon standard (ppm) or unknown</u>	<u>number of injections</u>	<u>average peak area (integrator counts)</u>	<u>standard deviation</u>
30.03	5	2.544 E5	1.5 E4
45.04	6	4.393 E5	1.3 E4
60.06	4	5.857 E5	1.4 E4
75.07	6	7.027 E5	2.7 E4
90.08	5	8.781 E5	2.7 E4
105.10	3	1.004 E6	1.1 E3
120.11	4	1.166 E6	1.5 E3
unk.# 4 (20/250 dilution)	5	5.398 E5	1.7 E4
unk.# 4 (20/250 dilution)	5	5.254 E5	7.3 E3

**TABLE 2.44**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (8/5/89)**

<u>concentration of silicon in the NBS ferrosilicon stan- dards (ppm) or unknown ferro- silicon</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.04	3	2.585 E5	2.1 E3
45.06	4	3.992 E5	1.3 E4
60.07	4	5.541 E5	8.9 E3
75.09	3	6.692 E5	5.8 E3
90.11	3	8.135 E5	1.5 E4
105.13	6	9.496 E5	1.7 E4
120.15	3	1.082 E6	6.4 E3
unk.# 3 (20/250 dilution)	4	3.015 E5	7.7 E3
unk.# 4 (20/250 dilution)	3	5.575 E5	1.8 E3
unk.# 4 (20/250 dilution)	4	5.789 E5	7.1 E3

**TABLE 2.45**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS SILICON STANDARDS**  
**AND UNKNOWN FERROSILICON SAMPLES (30/5/89)**

<u>concentration of silicon in the NBS silicon standards (ppm) or unknown ferrosilicon sam- ples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
60.06	4	5.725 E5	1.3 E4
75.09	3	6.819 E5	8.3 E3
90.11	4	8.461 E5	4.2 E3
120.15	4	1.150 E6	1.5 E4
unk. #4 (20/250 dilution)	4	5.806 E5	7.3 E3
unk. #4 (20/250 dilution)	5	5.804 E5	1.1 E4

**TABLE 2.46**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (6/6/89)**

<u>concentration of silicon in the NBS standards (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
45.06	4	5.072 E5	7.5 E3
60.07	4	6.872 E5	8.0 E3
75.09	4	8.687 E5	2.5 E4
90.11	4	1.028 E6	9.8 E3
105.13	5	1.229 E6	1.8 E4
unk.# 3 (20/250 dilution)	9	4.206 E5	1.8 E4
unk.# 4 (20/250 dilution)	7	7.466 E5	8.8 E3
unk.# 4 (20/250 dilution)	4	7.107 E5	3.1 E3

**TABLE 2.47**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (20/6/89)**

<u>concentration of</u> <u>silicon in the NBS</u> <u>standards (ppm) or</u> <u>unknown ferro-</u> <u>silicon samples</u>	<u>number of</u> <u>injections</u>	<u>average peak</u> <u>area (integra-</u> <u>tor counts)</u>	<u>standard</u> <u>deviation</u>
45.06	6	5.292 E5	9.7 E3
60.07	4	7.062 E5	8.6 E3
75.09	8	8.879 E5	1.7 E4
90.11	9	1.080 E6	2.7 E4
unk. # 3 (20/250 dilution)	6	4.418 E5	1.1 E4
unk. # 5 (20/250 dilution)	9	4.755 E5	1.3 E4
unk. # 5 (20/250 dilution)	5	4.814 E5	1.5 E4



**TABLE 2.48**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (21/6/89)**

<u>concentration of silicon in the NBS standards (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
45.06	3	5.066 E5	4.1 E3
60.07	6	6.738 E5	1.3 E4
75.09	3	8.722 E5	6.5 E3
90.11	4	1.024 E6	2.0 E4
unk. #4 (20/250) dilution	6	6.689 E5	6.9 E3

**TABLE 2.49**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (23/6/89)**

<u>concentration of silicon in the NBS standards (ppm) or unknown ferro- silicon</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.04	4	3.487 E5	6.2 E3
60.07	4	6.830 E5	1.4 E4
75.09	3	8.676 E5	4.4 E3
90.11	5	1.056 E6	2.5 E4
unk. # 3 (20/250 dilution)	6	3.989 E5	7.1 E3

**TABLE 2.50**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER OF**  
**INJECTIONS FOR THE PRETREATED NBS FERROSILICON SILICON**  
**STANDARDS AND UNKNOWN FERROSILICON SAMPLES (5/7/89)**

<u>concentration of silicon in the NBS standards (ppm) or unknown ferro- silicon</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.04	5	6.193 E4	1.2 E3
45.06	7	9.286 E4	2.4 E3
60.07	5	1.304 E5	2.7 E3
75.09	5	1.625 E5	3.2 E3
unk. # 3 (20/250 dilution)	5	7.769 E4	1.5 E3

**TABLE 2.51**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE PRETREATED NBS SILICON STANDARDS**  
**AND UNKNOWN FERROSILICON SAMPLES (19/7/89)**

<u>concentration of silicon in stan- dard (ppm) or unknown ferrosili- con samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
30.03	7	6.519 E5	2.3 E4
45.04	5	1.012 E6	2.1 E4
60.06	5	1.325 E6	2.2 E4
unk. #4 (20/250 dilution)	9	1.347 E6	5.1 E4
unk. #3 (20/250 dilution)	12	8.165 E5	2.6 E4

**TABLE 2.52**  
**THE AVERAGE PEAK AREA, STANDARD DEVIATION AND NUMBER**  
**OF INJECTIONS FOR THE PRETREATED NBS SILICON STANDARDS**  
**AND UNKNOWN FERROSILICON SAMPLES (29/7/89)**

<u>concentration of silicon in stan- dard (ppm) or unknown ferro- silicon samples</u>	<u>number of injections</u>	<u>average peak area (integra- tor counts)</u>	<u>standard deviation</u>
21.02	7	5.023 E5	1.2 E4
24.02	5	5.256 E5	9.4 E3
45.04	5	1.029 E6	2.8 E4
60.06	4	1.378 E6	2.5 E4
unk. #4 (20/250 dilution)	9	4.867 E5	2.7 E4
unk. #4 (20/250 dilution)	8	5.126 E5	2.6 E4