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USE OF AN "AUTOMATIC SULPHUR TITRATOR" IN ROCK AND MINERAL ANALYSIS: DETERMINATION OF SULPHUR, TOTAL CARBON, CARBONATE AND FERROUS IRON

(Report, 4 figures and 8 tables)

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ABSTRACT

An induction furnace and an automatic titrator have been applied to the iodimetric determination of sulphur in rocks. Total carbon has been determined in a slightly modified version of the same apparatus, involving a non-aqueous absorbing solution and titration system. The modified system has also been used to determine carbonate by titrating the carbon dioxide evolved by acid treatment. Finally, the same titrator has been utilized in the determination of ferrous iron by titrating the sulphur dioxide evolved when a rock sample is digested in a hot mixture of concentrated sulphuric and phosphoric acids.

RÉSUMÉ

On a mis au point une fournaise à induction et un appareil de titrage automatique pour le dosage iodimétrique du soufre dans les roches. Le carbone total a été dosé dans le même appareil, un peu modifié, en se servant d'une solution d'absorption et d'un système de titrage non-aqueux. Le système modifié a été mis au point aussi pour doser le carbonate en titrant le gaz carbonique dégagé par l'action d'un acide. Enfin, l'appareil a été utilisé pour le dosage du fer ferreux en titrant le gaz sulfureux dégagé quand un échantillon de roche est traité par un mélange chaud d'acides sulfurique et phosphorique concentrés.

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INTRODUCTION

The laboratories of the Geological Survey of Canada have been engaged for many years in the development of methods for the analysis of silicate rocks and minerals. The aim of that work has been to evolve analytical methods which are less time-consuming than classical procedures but more reliable than the many "rapid" schemes. The need to overcome the limitations of some existing methods has also been of interest. Further, there is the possible benefit that some of the newer methods might be more flexible, both in changing from one type of sample to another, and in varying the speed/accuracy balance by merely changing the degree of refinement of a given procedure. Under ideal conditions, such methods would permit a laboratory to produce "precise" and/or "rapid" analyses without the manual dexterity of a classical analyst on the one hand, or the expense of such equipment as a multichannel X-ray fluorescence spectrometer on the other.

Some progress has already been made toward these goals. Thus an atomic absorption scheme, based on a "lithium-fluoborate" sample treatment, has been described (Abbey, 1970a) for the determination of seven major components. Further work with the lithium-fluoborate system, using both colorimetry and atomic absorption, has led to improved precision for silica and extension of the method to at least five (possibly seven) additional minor elements. (Details will be given in a later publication.) An improved non-distillation method for fluorine and chlorine was described by Sen Gupta (1968). New methods for the determination of total carbon and carbonate (Sen Gupta, 1970b) and of sulphur (Sen Gupta, 1963, 1970a) have been described, but further improvements in speed and simplicity appeared desirable. Ferrous iron and "total water" methods (see Maxwell, 1968, p. 208-210, 217-223) also suffered from limitations, and some improvements were needed.

This paper describes the use of combinations of an automatic titrator, an induction furnace and two acid-evolution trains to methods for the determination of total sulphur, total carbon, carbonate ("carbon dioxide") and ferrous iron.

Acknowledgment

THE AUTOMATIC "SULPHUR" TITRATOR

This instrument is common to all of the methods described in this paper. Details of other apparatus are given in Appendix I.

The LECO fully automatic sulphur titrator, model 532, was designed for the determination of sulphur in steel. Sulphur dioxide, evolved by combustion, is absorbed by a solution containing hydrochloric acid, potassium iodide, starch indicator and sufficient potassium iodate to produce the desired blue colour. As the sulphur dioxide is absorbed, the indicator colour tends to fade. The

change is sensed by a photocell, which causes standard potassium iodate to be drawn from a burette to maintain the intensity of the blue colour. When no further sulphur dioxide is absorbed, no further titrant is delivered, and the burette reading gives per cent sulphur directly, provided the correct sample weight and titrant normality are used.

Details of the construction of the titrator and instructions for its use are given in the Laboratory Equipment Corporation (LECO) publication "Form No. 133A".

VERIFICATION OF THE METHODS

Normally the reliability of a new analytical method can be tested by analyzing standard samples, or by comparing results with those obtained by established methods.

Sulphur values are available in the compilations of analytical data for six American and three French samples of "standard rocks" (Flanagan, 1969; de la Roche and Govindaraju, in press), but the concentrations involved are very low (0.01 to 0.04 per cent). Further, the compilations report fewer than 10 sulphur results for each sample, compared to over 40 values per sample for such components as silica. The sulphur values that are listed are not in close agreement with one another. Carbon results for the reference samples are available in greater numbers, but agreement is no better.

To complicate matters further, some laboratories apparently do not distinguish "carbon dioxide", evolved by acid evolution and therefore representing carbonate, from the carbon dioxide produced by combustion, representing "total carbon". In Flanagan's (1969) compilation, the Geological Survey of Canada laboratory was the only one reporting non-carbonate carbon.

Ferrous iron values for the reference rocks are more plentiful, but there are still marked discrepancies, even between the "select laboratories" (Abbey, 1970b), that are in relatively good agreement for other components.

Standard samples of steels, slags and related materials are available from several sources. They are useful in checking the completeness of recovery of evolved sulphur dioxide or carbon dioxide, but are of no value in estimating the completeness of extraction of sulphur or carbon from rock samples.

The situation is no better in comparing results by proposed methods with those from older established procedures. Limitations of some of the older methods were among the prime reasons why this work was undertaken. For example, even as well established a conventional method as that of Pratt for ferrous iron (Maxwell, 1968, p. 416-419) has been known to yield a persistent negative bias.

For the above reasons, some of the data reported in the verification of these methods should be regarded as merely an indication of the limitations of such tests.

DETERMINATION OF SULPHUR

The first departure from the classical gravimetric determination of sulphur was introduced at the Geological Survey by Sen Gupta (1963). The method involved heating with vanadium pentoxide in a resistance furnace at 950°C. The evolved sulphur dioxide was absorbed in an excess of standard iodate-iodide solution and the excess back-titrated with standard sodium thiosulphate. When low results were obtained on some samples, the heating temperature was changed to 1450°C, the vanadium pentoxide was replaced by tin, and the combustion was done in a stream of oxygen. Later (Sen Gupta, 1970a), both speed and accuracy were improved by using induction heating with iron chips.

As a result of the work of Foscolos and Barefoot (1970), it appeared that the method could be made more rapid by using an automatic titrator. In everyday use, the manual back titration method was not only slow, but was also

subject to possible error, such as losses of sulphur dioxide by dissolution in water condensed in the apparatus. Sulphur dioxide losses were also possible in the absorption step. Manual control of oxygen flow rate was also a problem.

With the automatic titrator, complete absorption of the sulphur dioxide is assured by titrating it in the same container as fast as it is absorbed. The direct titration with potassium iodate (which can be weighed as a primary standard) simplifies calculation. A check-valve, built into the automatic titrator, permits use of a constant flow rate of oxygen. Water condensation in the delivery tube between furnace and titrator can easily be eliminated by winding a heating tape around the tube.

Details of the apparatus and the operating procedure are given in the Appendices. Table 1 lists results for a variety of materials, and comparison with other methods. With the exception of one of the iron ore samples, the results appear to be acceptable within the limits ordinarily required for rock analysis.

Sulphide is probably the form in which sulphur occurs in most of the samples in Table 1. In order to establish that sulphate sulphur is also recovered in the proposed method, samples of several reagent grade sulphates were analyzed. Recoveries of sulphur were low by four to seven per cent of the amount

Table 1

Sulphur Found in Various Samples

Sample No. and Type	S found, per cent Proposed Method	Others
LECO 501-503 (steel)	0.024, 0.026	0.025[a]
LECO 501-506 (steel)	0.023, 0.025	0.024[a]
BCR-1 (basalt)	0.04	0.04[b]
BR (basalt)	0.02_5, 0.03	0.02[c]
GA (granite)	0.00, 0.01	0.01[c]
GH (granite)	0.00, 0.00_5	0.00_5
B.C.S. 301 (iron ore)	0.41, 0.44, 0.37, 0.39, 0.40, 0.42, 0.44	0.47[d]
B.C.S. 303 (iron ore)	0.19, 0.19, 0.19, 0.19, 0.20, 0.20	0.22[d]
B.C.S. 174-1 (slag)	0.18, 0.18, 0.18 0.17_5, 0.19	0.16[d]
NBS 1A (limestone)	0.28, 0.27_5	0.27[e]
138-65 (sandstone)	1.10, 1.10	1.14[c]
140-65 (sandstone)	2.65, 2.67	2.70[c]

[a] Certificate value, Laboratory Equipment Corp.

[b] Proposed value (Abbey, 1970b).

[c] Induction furnace, manual titration, method of Sen Gupta (1970a).

[d] Certificate value, British Chemical Standards.

[e] Certificate value, U.S. National Bureau of Standards.

present. The losses were likely the result of the rapid evolution of sulphur dioxide from the samples (which averaged about 20 per cent sulphur) and hence incomplete absorption. The data in Table 1 also show a tendency toward incomplete recovery with increasing sulphur content.

Further refinement will be required if the method is to be applied to the high-precision determination of major amounts of sulphur.

DETERMINATION OF TOTAL CARBON AND CARBONATE

Sen Gupta (1970b) introduced a non-aqueous manual titration scheme for determining the carbon dioxide evolved from rock and mineral samples, either by combustion in an induction furnace ("total carbon") or by acid evolution ("carbonate carbon"). The carbon dioxide was absorbed in an acetone solution, containing monoethanolamine and a measured excess of a standard methanolic solution of sodium methylate. After absorption was completed, the excess sodium methylate was back-titrated with a standard methanolic solution of benzoic acid.

In everyday use, the manual titration methods for both forms of carbon were found to suffer from the same limitations as the corresponding method for sulphur. With the combustion method, there was the further hazard of possible ignition of the solvent vapours if they happened to be drawn back into the hot zone of the furnace.

Possible use of the automatic "sulphur" titrator for acid-base titrations is suggested in the instruction manual (LECO Form No. 133A). An attempt was therefore made to find a combination of operating parameters which would permit use of the titrator for the automatic determination of carbon dioxide.

In changing from the manual to the automatic titration method, the following modifications were needed:

(1) The absorbing liquid was changed from a solution of sodium methylate and monoethanolamine in acetone-methanol to a somewhat more concentrated solution of triethanolamine in acetone alone. However, because the acetone used is occasionally recovered by distillation, it is likely to contain some methanol, derived from the methanolic solution of sodium methylate used in earlier titrations. Enough sodium methylate is added before the titration to produce the desired colour in the indicator. The benzoic acid back-titrant is no longer required.

(2) The phenolphthalein indicator used in the manual back-titration method was replaced, first by a cresol red-thymol blue mixture, and later by thymolphthalein. The latter indicator changes from colourless to blue at a higher pH than the others, thereby facilitating retention of absorbed carbon dioxide. Further, the colour and its fading characteristics are very similar to those of the starch-iodine complex for which the apparatus is designed.

(3) As was done in the sulphur method, a heating tape was wound around the tube leading from the induction furnace, to prevent condensation of moisture that might absorb some carbon dioxide.

(4) Replacement of the magnesium perchlorate trap between the induction furnace and catalyst furnace (Sen Gupta, 1970b) by one charged with anhydrous calcium sulphate served to eliminate a tendency for the vinyl tubing leading from that tube to turn brown.

(5) A cooling fan was built into the titrator, to minimize evaporation losses and other effects of heat on the organic solvents. Some modification was also required in the acid-evolution train for the "carbonate carbon" determination. After the reflux condenser, which removes the bulk of the water, the gas stream passes through two

magnesium perchlorate traps to remove residual moisture. It then goes to a column containing, in succession, copper sulphate on a pumice base (to remove hydrogen sulphide), manganese dioxide (to remove sulphur dioxide) and cupric oxide (to remove any residual hydrochloric acid). Finally, any water derived from the reactions in the preceding column is removed by passing the gases through two more magnesium perchlorate traps before they go on to the titrator. Further details of the apparatus and procedure are given in the Appendices.

Sodium methylate cannot be weighed out as a primary standard, as can potassium iodate in the sulphur method. The titrant must therefore be standardized by analyzing samples of known carbon content (by combustion or acid evolution, as applicable). In order to make such standardization operations similar to actual analyses, a series of rock samples was calibrated, using both determinations.

A batch of sodium methylate solution was first standardized by running three LECO standard steel samples through the combustion scheme. Three Bureau of Standards steel samples and a sample of pure sodium carbonate were then analyzed, with the results shown in Table 2. Six rock samples, intended for use in future standardizations, were then analyzed in replicate by combustion, with the results shown in Table 3.

Table 2

Recovery of Carbon, Combustion Method

Sample	C, per cent Present	Found
LECO 501-503	0.17_1	Calibration
LECO 501-504	0.38_1	
LECO 501-506	0.85_9	
NBS 22	0.59_1	0.58
NBS 106	0.38_0	0.37
NBS 162	1.00_0	1.00
NBS 23	0.80_5	0.77
Na_2CO_3	11.33	11.3_4

Next, pure barium carbonate was used to standardize the titrant via the acid evolution scheme, and the resulting titre found to agree with that derived by combustion of the LECO samples, within 2 parts per 1000. The six rock samples listed in Table 3 were then analyzed in replicate by the acid evolution method, with results as shown in Table 4. Sample 1985 has been in use for several years as an "in house" reference for carbon dioxide determinations, with an assigned value of 2.02 per cent.

The six samples were further analyzed by a Mines Branch laboratory, using combustion in a resistance furnace, with equal weights of samples and vanadium pentoxide, and a gravimetric finish. Two of the samples were treated at two different temperatures. Results are compared with our own values in Table 5.

The Mines Branch results, obtained by combustion, are in good agreement with the Geological Survey results, obtained by acid evolution, but they show a persistent negative bias when compared with the Geological Survey

combustion results. For the two samples analyzed at two temperatures, the Mines Branch results are very slightly higher at the higher temperature. The higher values found in using the induction furnace may well be the result of the higher temperature. Fulton and Fryxell (1959), using an optical pyrometer, found that the temperature attained in an induction furnace may be as high as 1550°C, as is borne out by the fact that the iron chips melt. (The melting point of iron is 1535°C). The more efficient absorption of carbon dioxide in the automatic titrator (and the fact that it is titrated as it is absorbed) may also account for the higher results obtained by the proposed method.

Table 3

"Total Carbon" Found in Rock Samples

(for standardization use)

Sample	Total found, per cent (expressed as CO_2)	Mean	S.D.*
953	2.23, 2.20, 2.12, 2.19, 2.21	2.19	0.04
1057	0.80, 0.84, 0.86, 0.83, 0.85	0.84	0.02
1062	1.16, 1.18, 1.17, 1.21, 1.16	1.17	0.02
1069	0.94, 1.02, 0.99, 1.01, 0.97	0.98	0.03
1080	4.00, 4.07, 4.08, 4.10, 4.04	4.06	0.04
1985	2.14, 2.20, 2.21, 2.16, 2.20 2.15	2.17	0.03

* S.D. - Standard deviation

Table 4

"Carbonate Carbon" Found in Rock Samples

(for standardization use)

Sample	CO_2 found, per cent	Mean	S.D.
953	2.04, 2.03, 2.03, 2.01, 2.00	2.02	0.02
1057	0.80, 0.77, 0.81, 0.79, 0.82	0.80	0.02
1062	1.10, 1.17, 1.11, 1.12, 1.10	1.12	0.03
1069	0.86, 0.89, 0.86, 0.87, 0.89	0.87	0.01
1080	3.62, 3.50, 3.74, 3.19*, 3.68, 3.64, 3.75	3.66	0.09
1985	2.07, 1.96, 1.99, 2.04	2.02	0.05

* Not included in calculation of mean

The methods were finally tried on seven international reference samples (Table 6). The acid evolution results obtained by automatic titration are low in the case of three samples (GA. GH and GSP-1). However, the absolute deviations are not very great, being comparable to those found for the much higher carbon contents involved in Tables 2, 3, 4 and 5. Good recovery of evolved carbon dioxide appears assured by the values in those tables, and incomplete evolution

of carbon dioxide is highly unlikely, either at the high temperature of the induction furnace or on prolonged boiling with hydrochloric acid. It might then be deduced that the proposed method becomes less reliable at lower levels. However, as pointed out above, the assigned values for the reference samples are far from certain. It can only be concluded that, for relatively low carbonate contents, results by the proposed method are probably no worse than by older methods.

Table 5

CO_2 Determinations - Comparison Between

Laboratories and Methods

Samples No.	Mines Branch Resistance Furnace		Geological Survey	
	1100°C	1200°C	Induction Furnace	Acid Evolution
953	2.03		2.19	2.02
1057	0.78	0.80	0.84	0.80
1062	1.10		1.17	1.12
1069	0.89		0.98	0.87
1080	3.73	3.76	4.06	3.66
1985	2.07		2.17	2.02

Table 6

"Carbon" Determinations on International Reference Samples by Different Methods

(All results expressed as per cent CO_2)

Sample No.	Total Carbon			Carbonate Carbon			
	Resist. Grav.	Induct. Manual	Induct. Automat.	Expected*	Acid Grav	Acid Manual	Acid Automat.
BR	1.00	0.94	1.14	0.86	0.82	0.83	0.89
DTS-1		0.08	0.11	0.06	0.01	0.07	0.08
G - 2		0.08	0.07	0.08	0.10	0.08	0.11
GA	0.17	0.18	0.21	0.11	0.08	0.06	0.05
GH		0.19	0.28	0.14	0.18	0.11	0.06
GSP-1	0.12	0.12	0.09	0.12	0.13	0.10	0.07
PCC-1		0.18	0.17	0.16	0.10	0.18	0.17

* Ref. Abbey, 1970b; de la Roche and Govindaraju, in press.

DETERMINATION OF FERROUS IRON

Two methods for determining ferrous iron in silicate rocks and minerals have been used at the Geological Survey laboratories for some years. In the older "modified Pratt" method (Maxwell, 1968, p. 419), the sample is decomposed by gentle heating with hydrofluoric and sulphuric acids in a lightly-covered platinum crucible. After decomposition is completed, the solution is quickly mixed with another solution containing sulphuric and boric acids, and the ferrous iron titrated potentiometrically with dichromate. In the more rapid "modified Wilson" method (Maxwell, 1968, p. 419-421), several samples are decomposed simultaneously at room temperature, by means of hydrofluoric acid, in the presence of ammonium vanadate, in covered polyethylene flasks, on an oscillating device. Ferrous ions, as they are released, reduce some of the vanadate ions. After decomposition is completed, the solution is mixed with sulphuric, phosphoric and boric acids. Excess ferrous ammonium sulphate is added to reduce the remaining vanadate, and that excess titrated with dichromate.

Both of the above methods have limitations. The older method requires very careful attention to detail. The "rapid" method is subject to errors of uncertain magnitude, necessitating the use of correction factors based on the analysis of control samples. Neither method completely decomposes pyrite or chromite, both of which may account for a significant fraction of the ferrous iron content of some rocks.

A different method has been in use for the determination of ferrous iron in chromite. Based on the work of Seil (1943), it involves digestion of the sample at a high temperature in a mixture of concentrated phosphoric and sulphuric acids. Ferrous iron in the sample reduces a stoichiometric quantity of sulphuric acid, yielding sulphur dioxide. The evolved gas is led into a solution of potassium dichromate. After decomposition is completed, the unreacted dichromate is reduced by the addition of excess ferrous ammonium sulphate, and that excess titrated with more dichromate.

After the automatic titrator had been applied to the sulphur, total carbon and carbonate determinations, it occurred to one of the authors (J.L.B.) that the same instrument might be suitable for the iodimetric titration of the sulphur dioxide evolved in the phosphoric-sulphuric digestion method for ferrous iron. There was some question whether the method, designed for use on an oxide mineral, would be equally effective with silicates.

Considerable modification was found to be necessary, both in the apparatus and the operating parameters. The 200-ml round-bottom flask (Seil, 1943) was replaced by a test-tube shaped reaction vessel (see Appendix I), which permits more rapid decomposition. A reflux condenser and a sulphuric acid trap were introduced between the reaction vessel and the titrator, to minimize the carry-over of water and sulphuric acid. Addition of a few drops of water to the sample before introducing the acid mixture was found to facilitate initiation of the decomposition reactions. Either nitrogen or carbon dioxide, under slight positive pressure, may be used as carrier gas. For most rocks, the decomposition is carried out at a higher temperature than that used by Seil (1943) for chromite, but the digestion period is shorter. After decomposition is completed, a white gelatinous residue remains in the reaction vessel. If the heating period is too short, unreacted particles of resistant ferrous-bearing minerals can readily be seen as dark specks, which can easily be decomposed by heating several minutes longer.

As with other methods for ferrous iron, serious interference occurs if any oxidizable matter is present. In rock samples, sulphides are the most serious offenders. The maximum tolerable sulphur content is not easily specified, as it will depend on the chemical state of the sulphur - sulphates, for example, being harmless. Unlike other methods, the one now proposed completely decomposes pyrite. The additional ferrous iron thus released serves to diminish the negative error of other methods, but the sulphur released introduces a multiple positive error: sulphur dioxide is produced both by the oxidation of the

Table 7

Ferrous Iron Found in Rock Samples

Sample No. and Type	FeO found, per cent Proposed Method	Others
G-1 (granite)	0.95	0.97[a]
W-1 (diabase)	8.75	8.77[a]
AGV-1 (andesite)	1.95, 2.01, 1.98, 2.02, 1.98	2.02[b]
BCR-1 (basalt)	8.94, 8.89, 9.09, 8.82, 9.03	8.97[b]
DTS-1 (dunite)	7.23, 7.14, 7.33, 7.17, 7.32	6.98[b]
G-2 (granite)	1.24, 1.56, 1.45, 1.36, 1.40	1.45[b]
GSP-1 (granodiorite)	2.65, 2.64, 2.79, 2.76, 2.67	2.34[b]
PCC-1 (peridotite)	5.33, 5.20, 5.44, 5.35, 5.37, 5.44	5.14[b]
BR (basalt)	7.26, 7.21, 7.36, 6.97, 7.02	6.57[c]
GA (granite)	1.57, 1.47, 1.62, 1.56, 1.60	1.35[c]
GH (granite)	1.08, 1.09, 1.08, 1.02, 1.12	0.84[c]
Mica Fe (biotite)	19.68	19.17[c]
Lab 1 (basalt)	7.93, 7.90, 7.96, 7.93, 7.93, 7.91	7.97[d]
P2A (picrite)	9.08, 9.36, 9.31, 9.36, 9.31, 9.39	9.35[e]
Sample (granite)	0.70, 0.84, 0.70, 0.72, 0.72, 0.78	–

[a] Recommended value (Fleischer, 1969)

[b] Proposed value (Abbey, 1970b)

[c] Recommended value (de la Roche and Govindarju, in press)

[d] Conventional method

[e] Tentative value, based on many determinations

Table 8

Comparison of Ferrous Oxide Values
(all expressed as FeO, per cent)

Sample No.	This Work (mean)	Goldich et al.	"Best Laboratories" mean	"Best Laboratories" range
AGV-1	1.99	2.15[a]	2.02[c]	1.87-2.15[c,d]
BCR-1	8.96	9.17	8.97	8.73-9.17
DTS-1	7.24	7.48	6.98	6.78-7.48
G-2	1.40	1.56	1.45	1.31-1.56
GSP-1	2.70	2.53	2.34	2.23-2.53
PCC-1	5.32	5.51	5.14	4.88-5.51
BR	7.16	6.76[b]	6.61[b]	6.30-6.81[b]
GA	1.56	1.37	1.35	1.25-1.42
GH	1.08	0.92	0.83	0.72-0.93

[a] Goldrich, Ingamells, Suhr and Anderson (1967)

[b] Roubault, de la Roche and Govindaraju (1968)

[c] Abbey (1970b)

[d] Flanagan (1969)

sulphur from the mineral and by reduction of sulphate from the acid. It may be possible to evolve a stoichiometric correction, but more thorough study of the behavior of pyrite will be necessary before that can be done.

Details of the apparatus and procedure are given in the Appendices.

A number of international reference samples and laboratory "standards" were analyzed by the proposed method, most of them in replicate. Results are compared with those from other methods in Table 7. While agreement with other results is good for some samples, it is less satisfactory for others. Among the more conspicuous discrepancies are the results on DTS-1 and PCC-1, both of which are known to contain chromite. One of the laboratories which contributed data for both the American (Flanagan, 1969) and French (Roubault, et al., 1968) reference samples, is known to have used a special technique to correct for the effect of chromite in the conventional method (Goldich et al., 1967), and their results for FeO are conspicuously higher than the "proposed values", which are based on means of values reported by the "best laboratories" (Abbey, 1970b). Admittedly, the results of Goldich et al., are generally higher than those from the other laboratories even for some samples having no significant chromite content, although the differences are generally not as great as those where chromite is present. Some idea of the problem of correlating ferrous iron data may be deduced from Table 8, where the means of values obtained by the method now proposed are compared with those of Goldich et al., and with the means and ranges of values reported by the "best laboratories" (Abbey, 1970b). For half of the American samples, the proposed method shows a positive bias, relative to the "proposed values", but five of the six values are lower than those of Goldich et al. For all of the French samples, the proposed method is positively biased relative to both other values.

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Figure 1. General view of apparatus. GSC photo 201951-A

APPENDIX I

Apparatus

A general view of the apparatus for all four methods is shown in Figure 1. Reading from left to right, the components are:

   (a)   the special apparatus designed for digesting samples for ferrous iron determination and removing entrained water and sulphuric acid from the evolved sulphur dioxide;

   (b)   the LECO fully automatic sulphur titrator, model 532;

   (c)   the LECO two-tube high-frequency induction furnace, model 522 (left side in sulphur mode, right side in carbon mode);

   (d)   another LECO model 532 titrator, modified for carbon titration; and

   (e)   a carbon dioxide evolution train.

The combination of (a) and (b) is used for ferrous iron determination; (b) and (c) for sulphur; (c) and (d) for total carbon; and (d) and (e) for carbonate carbon. All of the apparatus is shown on an open work bench in Figure 1, but in actual operation, item (a) must be used in a fume hood. A line diagram of the entire assembly is shown in Figures 3 and 4.

The modular nature of the apparatus permits considerable flexibility. Thus if only ferrous iron and carbonate are required (as is the case in most ordinary rock analyses), the induction furnace and possibly one of the titrators may be omitted. At the opposite extreme, the addition of two more titrators would permit all four determinations to be done simultaneously. Many intermediate arrangements are also possible.

Item (a), the special apparatus for the ferrous method, is shown separately on a larger scale in Figure 2. The reaction vessel is made from a 24/40 standard taper female glass joint and is supported by springs. Its overall length is 150 mm. For most efficient digestion of the sample, the bottom of the reaction vessel is flattened to a diameter of about 15 mm, with rounded corners where the flattened surface meets the vertical walls.

The special heating mantle for the reaction vessel was prepared as follows: Nichrome wire (0.81 mm diameter) was wound around a 150 mm-length of a closed-end alumina tube (similar to Coors AD-998COE, 32 mm i.d.), leaving about 2 mm clearance between windings. The wire was coated with Saureisen Cement No. 33, and the leads connected to a 110-volt Powerstat variable transformer. The wired alumina tube was then surrounded by a larger tube (such as Coors AD-998COE, 38 mm i.d.), and the two tubes sealed together with the same cement. The Powerstat was adjusted to provide a working temperature of 430°C inside the inner ceramic tube, using a thermocouple. In Figures 1 and 3, the delivery tube from the left side of the induction furnace is shown connected to the input of the automatic titrator. For ferrous iron determination, that connection is broken, and the plastic delivery tube from the upper end of the reflux condenser is connected to the titrator input. A similar change is required in changing the other titrator from carbonate to total carbon determination.

Items (b) and (d), the automatic "sulphur" titrators are described in more detail in LECO Form No. 133A. Installation of the cooling fan is the only modification required in item (d) to make it suitable for carbon dioxide titration, but there are important changes in operating technique, as described below under "Procedures".

Item (c) is in effect two induction furnaces in one case, in that the two sides are entirely independent of one another, and can be operated simultaneously in the same or in different modes. Lower-priced single-tube and double-tube models are also available. In the latter case, only one tube can be operated at a time, but it is possible for one side to be in operation while the

other is being charged for another analysis. In this work, the sulphur mode of the induction furnace was arranged entirely as in the instruction manual, LECO Form 233C. The carbon mode involved a slight departure from Form 233C in that the Cloth Filter Dust Trap was replaced by the trap charged with anhydrous calcium sulphate.

Item (e) is based on the apparatus described by Maxwell (1968, p. 431) and Sen Gupta (1970b), modified somewhat as described above under "Determination of Total Carbon and Carbonate".

Additional traps, flowmeters and other components of the entire apparatus assembly are shown in Figures 3 and 4.
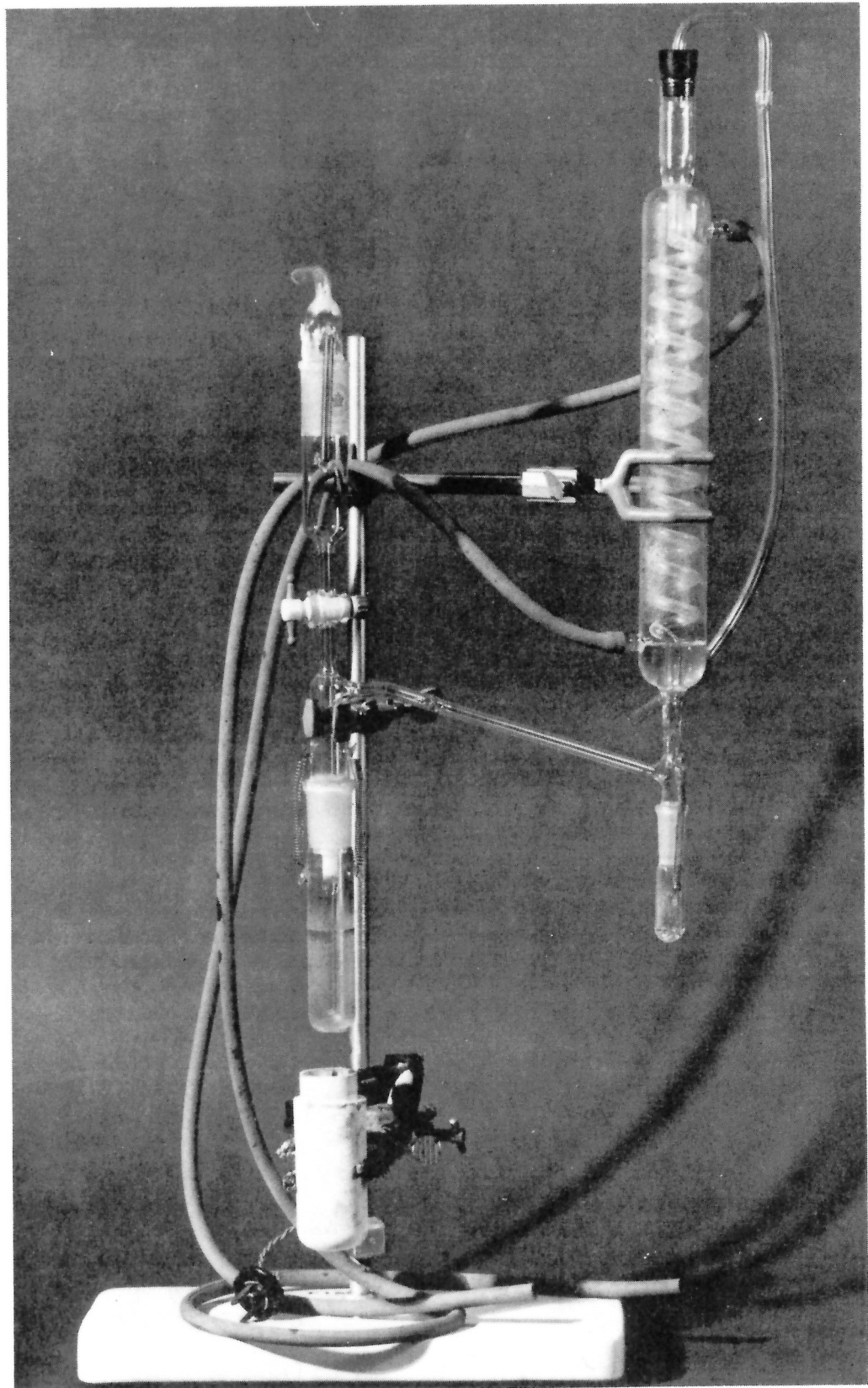
Figure 2. Close-up view of special apparatus for determination of ferrous iron.
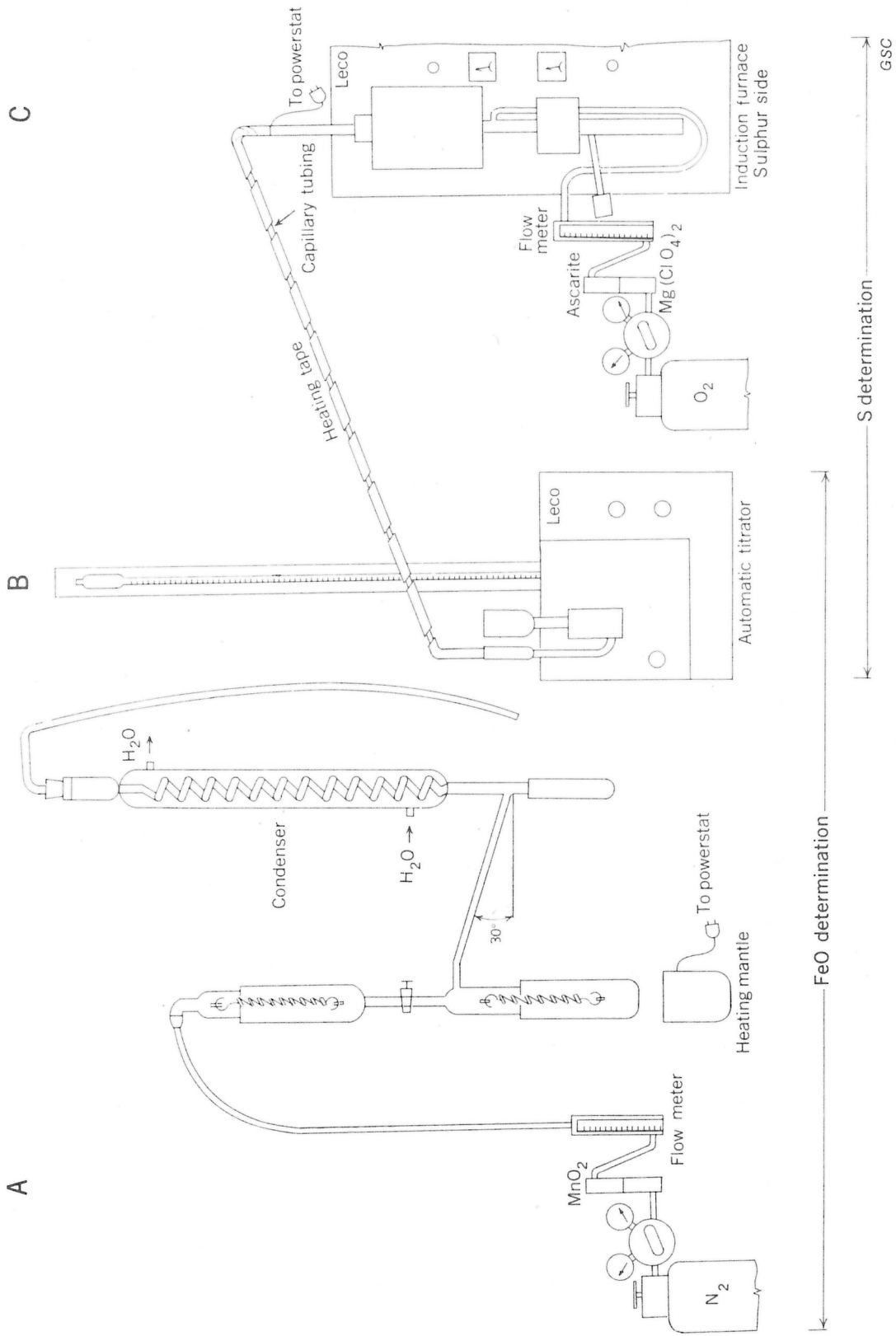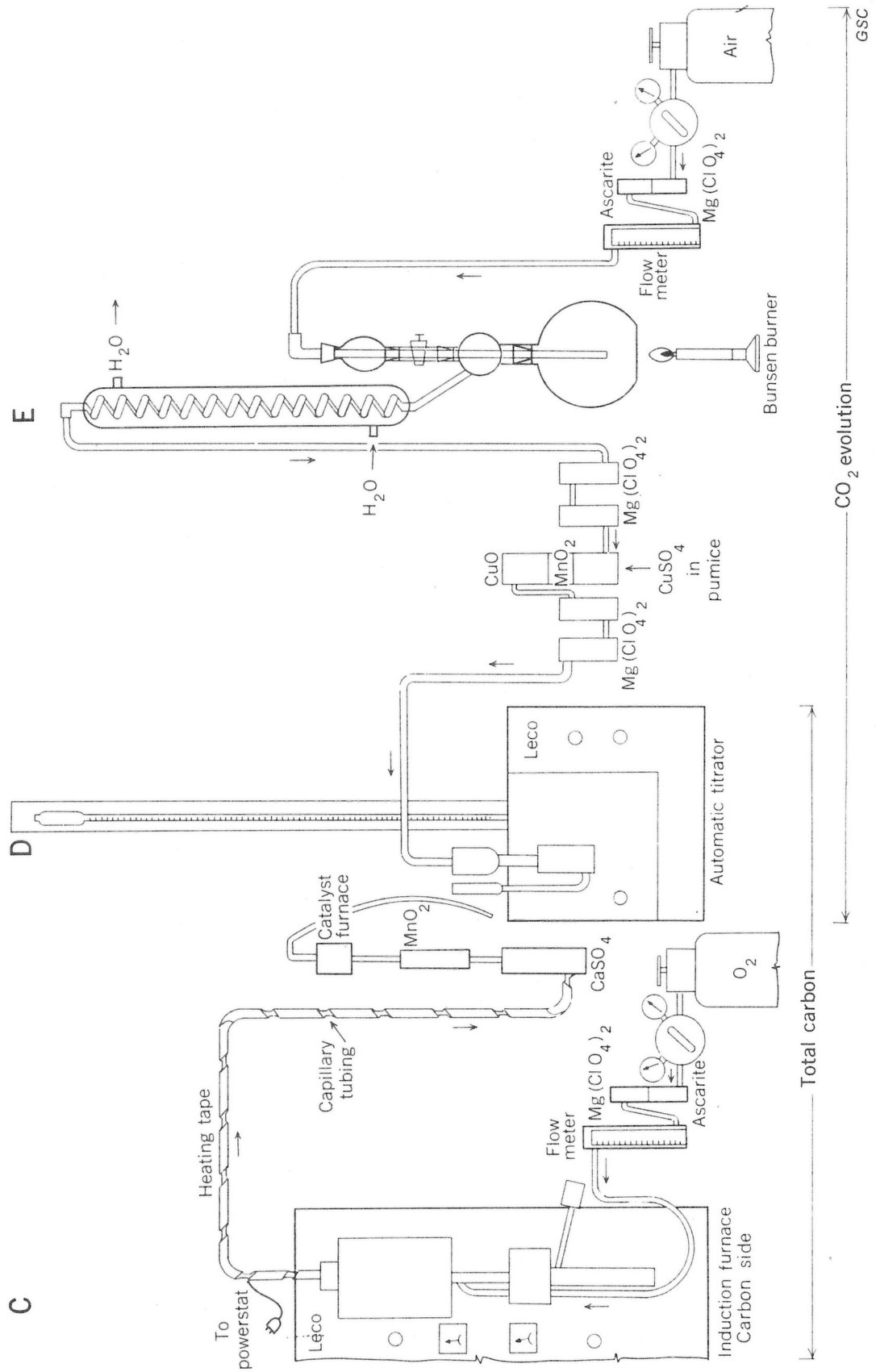GSC photo 201956

Figure 3. Line diagram, "sulphur side".

Figure 4. Line diagram, "carbon side".

APPENDIX II

Operating Procedure for Sulphur Determination

Apparatus and Reagents

In addition to the apparatus described in Appendix I, the following items are required:

1. **Combustion Crucibles**

    LECO 528-35 heavy duty crucible, equipped with porous covers, LECO 528-42, or equivalent.

2. **Standard Potassium Iodate**, 0.888 g per litre, containing one drop of Leconal wetting agent. (By using an iodate solution at double the strength recommended by LECO, and reducing the sample weight by a factor of five, the burette range is changed from 0.0-0.2 per cent to 0.0-2.0 per cent sulphur.) Store in the iodate reservoir bottle (LECO Form 133A, Fig. IV).

3. **Absorbing Solution**, 0.18N hydrochloric acid

    Dilute 30 ml of concentrated acid with water to a final volume of 2 litres. Store in the hydrochloric acid reservoir bottle (as in reference for solution 2.)

4. **Iodide-Starch Solution**

    Prepare as in LECO Form 133A, pp. 3-4. (B.D.H. "ANALAR" Soluble Starch has been found to be an acceptable substitute for Arrowroot starch.)

Method

The working procedure is based entirely on the instruction in LECO Forms No. 133A and 233C, available to all users of LECO equipment. Suitable modification would be required where other types of equipment are used. This procedure therefore specifies only those features which differ from the LECO instructions. The normal sample weight is 0.2 g, and 1.5 g Iron Chips, LECO 501-077 (or equivalent) are mixed with the sample in the crucible. If the sulphur content is between 2 and 4 per cent, the titration can be manually accelerated to the end of the burette's calibration range and the burette refilled with standard iodate while the sulphur dioxide is being absorbed, thereby doubling the working range. Alternatively, the sample weight can be reduced. The quantity of iron chips used may also require some variation, depending on the condition of the inductor coils in the furnace, in order to attain the operating conditions recommended in the instruction manual. Unless the sulphur contents being determined are unusually high, it is possible to use one charge of absorbing solution for a number of successive titrations. However, when the level of the increased volume of absorbing solution comes within less than 1 cm of the upper inlet port, the solution should be discarded and the vessel refilled with a fresh charge.

APPENDIX III

Operating Procedures for Total Carbon and Carbonate Determination

Apparatus and Reagents

In addition to the apparatus described in Appendix I, the following items are required:

1. #### Combustion Crucibles

   LECO 528-35 heavy duty crucibles, equipped with <u>perforated</u> covers, LECO 528-40, or equivalent.

2. #### Standard Sodium Methylate, 2.2g per litre of methanol.

   Dissolve 2.2g of sodium methylate in methanol and dilute to one litre with methanol. Solid sodium methylate deteriorates rapidly if exposed to air. On opening a 100-g bottle, it is advisable to transfer the contents quickly to small bottles containing 3-5g each, to seal the bottles and to open each only to weigh out the required 2.2g. Store the solution in a one-litre polyethylene reservoir bottle attached to the titrator in the same way as is the glass reservoir bottle for potassium iodate in the sulphur method.

3. #### Absorbing Solution (12 ml triethanolamine per litre of acetone).

   Dissolve 12 ml of triethanolamine in acetone and dilute to one litre with acetone. (The solution is not indefinitely stable, and should be prepared only in sufficient quantity for immediate use. It should be discarded if it turns yellow. The acetone used may be either fresh or recovered by distillation from the methanol-acetone mixture accumulated from previous titrations.) This solution is not pumped from its reservoir bottle to the titrating vessel, in order to avoid contact with rubber or vinyl tubing. For use, about 100 ml are poured into the absorption vessel.

4. #### Thymolphthalein Indicator

   Dissolve 0.5g thymolphthalein in 100 ml of methanol, add 3 pellets of sodium hydroxide and stir to dissolve. Three millilitres of this solution are added with each charge of absorbing solution.

<u>Notes:</u> (1) It has been observed that quantitative absorption of the carbon dioxide from a sample, by the absorbing liquid, is complete only if that liquid has already absorbed some carbon dioxide. It is therefore necessary to "condition" each charge of absorbing liquid by taking about 40 mg of pure calcium carbonate through the procedure (by combustion or acid evolution). The "conditioned" absorbing solution can then be used to absorb the carbon dioxide from a number of samples, subject to the same limitation as in the corresponding operation in the sulphur method. When the volume of liquid in the absorbing vessel becomes too great, only about one half of the solution should be discarded. More samples can then be analyzed without further "conditioning" of the absorbing solution. When the level of solution in the absorbing vessel again approaches the input opening, the entire solution should be discarded, a fresh charge added, and taken through the "conditioning" step.

(2) At the beginning of each working day (and for every fresh batch of sodium methylate solution), the titrant must be standardized by carrying two control samples (see Tables 3 & 4) through the procedure being used (combustion or acid evolution). Two or three additional control analyses should be performed in the course of a day of continuous operation.

(a)   Total Carbon (combustion)

As is the case with the sulphur method described in Appendix II, this procedure describes only those features which differ form the LECO instructions. The normal sample weight is 0.5g, and the sample is mixed in the crucible with 0.5g vanadium pentoxide and 1.5g Iron Chips, LECO 501-077 (or equivalent). For samples containing over 2 per cent carbon dioxide (or its equivalent as "total carbon"), the same alternative procedures are possible as in the case of samples containing relatively large amounts of sulphur. The weight of iron chips used may also require variation, as in the sulphur method. The blue colour of the indicator in the absorbing solution should be adjusted to give an absorbance of about 0.4 when measured in a 1-cm cuvette in a spectrophotometer at 600 nm, but this requirement may vary somewhat from one instrument to another. The percentage of total carbon in the sample (generally expressed as carbon dioxide for purposes of subtracting the carbonate carbon) is found by multiplying the burette reading by the factor derived from the analysis of control examples.

(b)   Carbonate Carbon (carbon dioxide by acid evolution)

Operation of the automatic titrator is the same as for total carbon determination. The acid-evolution procedure is based on that of Maxwell (1968, p. 432), the major difference being the use of compressed air at 0.5 lb./sq. in. at the input end of the apparatus, instead of suction at the outlet.

Weigh 0.5g sample into the reaction flask and add about 35 ml freshly-boiled and cooled water. Attach the flask to the apparatus train and pour 30 ml HCl (1:1) into the separatory funnel. Open the stopcock of the separatory funnel, allowing the acid to mix with the sample, and immediately connect the compressed air source to the top of the separatory funnel. The compressed air should be supplied at about 2 lb. per sq. in. pressure, and a flow rate of 350cc per min. These parameters may require variation from one instrument to another. Heat the contents of the flask to boiling and continue for 2-3 minutes, after which no further titrant should be flowing from the burette.

APPENDIX IV

Operating Procedure for Ferrous Iron Determination

Reagents

1. **Acid Mixture** (sulphuric-phosphoric)

   Mix 100 ml of concentrated sulphuric acid and 400 ml of syrupy phosphoric acid in a large beaker. Heat the uncovered beaker over a Meker burner. (The solution will come to a boil, but will subsequently begin to fume.) Fume strongly for 15 minutes. Allow to cool until fumes subside, then transfer to a pre-warmed all-Pyrex wash bottle. Store at about 100°C. The solution is dispensed warm, through the "blow tube" of the wash bottle. HANDLE WITH CARE!

2. **Carrier Gas**

   Nitrogen (or carbon dioxide), delivered at 1 lb./sq. in. at a flow rate of 1 litre/min.

3. **Standard Potassium Iodate**, 0.298g per litre

   Aside from the change in concentration, prepare and store in the same way as for the sulphur method.

4. **Absorbing Solution**, 0.18N hydrochoric acid

5. **Iodide-Starch Solution**

   Prepare solutions 4 and 5 in the same way as solutions 3 and 4 in the sulphur method.

Method

Operation of the automatic titrator is carried out in the same manner as for sulphur determination, except that it is frequently necessary to refill the burette several times during a titration, and a fresh charge of absorbing solution and indicator should be used for every sample.

Before beginning an analysis, turn on the carrier gas and cooling water and adjust the automatic titrator. The standard-taper joints should be coated with a thin layer of phosphoric acid as a sealant.

Weigh 0.2g sample (less if the sample contains more than 6 per cent FeO) into the reaction vessel, moisten with a few drops of water and attach the vessel to the apparatus. Rotate the joint to ensure a tight seal and secure with springs. (The sulphuric acid trap under the condenser must be similarly sealed and secured). Place 25 ml of the acid mixture in the dropping funnel, insert the gas inlet tube, open the funnel stopcock and secure the inlet with springs. Surround the reaction vessel with the heating mantle, (set to give 430°C) and heat for 15 minutes.

Lower the heating mantle and check the reaction vessel for undecomposed material. If any is present, replace the heating mantle and continue heating until decomposition is complete.

At the end of an analysis, the reaction vessel should be removed from the apparatus and allowed to cool somewhat before its contents are discarded. The reaction vessel is then scrubbed with a test-tube brush to remove the gelatinous residue, rinsed thoroughly with warm tap water, followed by distilled water, and dried in an oven. The contents of the sulphuric acid trap under the condenser should be emptied after every analysis.

At the end of a day's work, the inside surfaces of the dropping funnel, delivery tube and condenser should be rinsed thoroughly with distilled water, and allowed to drain dry over-night. On starting in the morning, a blank should be analyzed to stabilize the apparatus (removal of residual traces of water, etc.), then a second blank taken through the procedure to provide a correction for subsequent analyses.

    Repeated digestion with hot phosphoric acid will eventually wear away the delivery tube which is immersed in the acid, and also the walls of the reaction vessel. Both should be examined daily for wear, and replaced if necessary. A stock of 10 or 12 reaction vessels can be used in rotation. In actual use, delivery tubes made of fused silica have been found to be more resistant to phosphoric acid than those made of borosilicate glass.

    For a 200-mg sample and the potassium iodate concentration specified above, the percentage of FeO is found by multiplying the burette reading by 15, with corresponding adjustment for other sample sizes.