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## **Rapid Direct and Simultaneous Determination of CO<sub>2</sub> and FeO in Carbonate and Silicate Analysis**

by *B. Ayranci*, Zürich<sup>1)</sup>

### **Abstract**

The simultaneous analysis of carbon and ferrous iron can be carried out after the dissolution of the sample by means of a non-oxidizing acid disintegration procedure. The CO<sub>2</sub> is determined gravimetrically or by non aqueous titration. FeO is analyzed by volumetrical methods.

The simultaneous determination of iron and carbon can be routinely completed in a silicate and carbonate analysis. This is possible because both inorganic carbon and ferrous iron are determined in a similar-non-oxidizing-environment while the total CO<sub>2</sub> (inorganic + organic carbon) is analyzed after an oxidizing procedure.

The Analysis of CO<sub>2</sub> and FeO in geochemical samples is mostly performed in two different analytical steps:

### **1. DETERMINATION OF CO<sub>2</sub>**

The CO<sub>2</sub> is liberated from the sample either by combustion or by an acid disintegration procedure. The subsequent determination of CO<sub>2</sub> is carried out according to the individual equipments of laboratories in several ways, including by gravimetical, gaschromatographical, coulometrical, or indirect volumetrical methods (e.g. BOUVIER et al., 1972; HERRMANN, 1975; JEFFERY et al., 1960; JEFFERY et al., 1964; MEYROWITZ, 1970; RILEY et al., 1959).

The combustion technique or disintegration of the sample by means of oxidizing acids (such as HNO<sub>3</sub>, HNO<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> + CrO<sub>3</sub>) under an oxygen-stream is used to recover the total amount of CO<sub>2</sub> (inorganic carbon + organic matter) in carbonate and silicate samples (e.g. HILLEBRAND et al., 1953; JEFFERY et al., 1960).

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If only the inorganic carbon has to be determined, the powder is decomposed with diluted non-oxidizing acids (e.g. HCl, HCl + HF, H<sub>3</sub>PO<sub>4</sub>). The determination of the inorganic carbon and the total carbon is performed step by step (from the sample) by means of an acid disintegration procedure: The inorganic carbon is recovered just after disintegrating the sample with H<sub>3</sub>PO<sub>4</sub>. A suitable oxidizing acid (e.g. HNO<sub>3</sub>, CrO<sub>3</sub>) is added to the sample solution. The solution is boiled in order to destroy organic matter and to evolve CO<sub>2</sub> from the organic impurities. The total carbon is calculated after absorption and determination of the organic carbon.

## 2. DETERMINATION OF FeO

The determination of FeO is performed by a further analytical procedure: The sample is dissolved in a non-oxidizing environment by means of an acid treatment.

The sample solution is produced commonly by adding HF, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or (COOH)<sub>2</sub> etc. alone or combined together (e.g. HF + H<sub>2</sub>SO<sub>4</sub>, HF + H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub>).

The FeO concentration is recovered either by means of direct or indirect analytical methods (ALIMARIN et al., 1965; AYRANCI, 1976; BOUVIER et al., 1972; MAXWELL, 1968; PECK, 1964; WILSON, 1960).

The basic problems of the rapid direct and simultaneous determination of CO<sub>2</sub> and FeO from carbonate and silicate samples are:

- The selection of a suitable acid or acid combination for the dissolution of the sample.
- The complete dissolution of the sample without any oxidation before determining FeO and inorganic carbon.
- Quantitative and selective absorption of CO<sub>2</sub>.
- Retention of the oxidation state of iron.

The selection of an acid or acid combination for these purposes is limited, because:

The diluted HCl (as 1 + 1 or 1 + 2), which is widely used for the determination of inorganic carbon in easy soluble samples (e.g. calcite, limestone), may not dissolve quantitatively Fe- and Mg-rich carbonates or certain scapolites. Due to its relatively low boiling point, HCl can not be heated for a prolonged time to dissolve the samples at higher temperatures. A direct determination of FeO from a solution, which is disintegrated by HCl, is also complicated. At higher temperatures, the sample is disintegrated by HCl in sealed tubes or in autoclaves usually by adding a further acid (e.g. HCl + HNO<sub>3</sub>, HCl + H<sub>2</sub>SO<sub>4</sub>, HCl + HF). From a hydrochloric acid sample disintegration procedure, the FeO

determination is commonly carried out by means of indirect volumetric methods (e.g. HEY, 1941; JEFFERY et al., 1960).

H<sub>2</sub>SO<sub>4</sub>, which is also used widely for the disintegration procedure of the carbonates, oxides, silicates etc., has a considerably higher boiling point than HCl. It is used diluted as a non-oxidizing acid. At higher temperatures, concentrated H<sub>2</sub>SO<sub>4</sub> acts as an oxidizing acid due to the evolution of S, SO<sub>2</sub>, H<sub>2</sub>S during the dissolution of the samples (e.g. BOCK, 1972; DOLEŽAL, 1966).

H<sub>3</sub>PO<sub>4</sub> is used with its relatively high boiling point for the disintegration of ore minerals, silicates etc, when determining the concentration of FeO and CO<sub>2</sub>. For these purposes, the concentrated H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> is used (e.g. BOCK, 1972; BOUVIER et al., 1972; DOLEŽAL, 1966).

During the prolonged heating of the sample by means of the concentrated H<sub>3</sub>PO<sub>4</sub>, the reduction processes may occur (FUNKE et al., 1969). Furthermore, if the disintegrating procedure is carried out above 300 °C in a glass-vessel, the glass is seriously attacked.

According to the advantages and disadvantages of the several acids cited above, it seems justified to use a HF + H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> diluted acid combination at lower temperatures for the disintegration of the carbonates and silicates samples.

The disintegration procedure is carried out under a nitrogen stream in a CO<sub>2</sub> apparatus. The liberated CO<sub>2</sub> is absorbed and weighed or recovered titrimetrically; FeO may be determined either colorimetrically or volumetrically using KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

## Analytical Procedure

### A. Apparatus

For the analysis of CO<sub>2</sub> and FeO, the sample is disintegrated under a N<sub>2</sub> flow by means of HF + H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> in a CO<sub>2</sub> apparatus (fig. 1), which is modified after MEYROWITZ (1970). It consists of the following 3 units:

#### I. FLOW RATE REGULATION AND PURIFICATION OF NITROGEN

The analytically pure nitrogen flows through absorbers, which remove impurities such as O<sub>2</sub>, CO<sub>2</sub>, S and organic traces, before the gas enters the disintegration vessel. This unit is composed of the following pieces:

1. A gas wash bottle (250 ml), filled with 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> (dissolved in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in order to absorb H<sub>2</sub>O and SO<sub>2</sub> traces of nitrogen and preregulate the flow. It is connected to the N<sub>2</sub> cylinder by regulating units.
  - 1a A non-return valve.
2. A gas wash bottle (250 ml), filled with molecular sieve 13 × or 5A, which absorbs CO<sub>2</sub> and H<sub>2</sub>O.



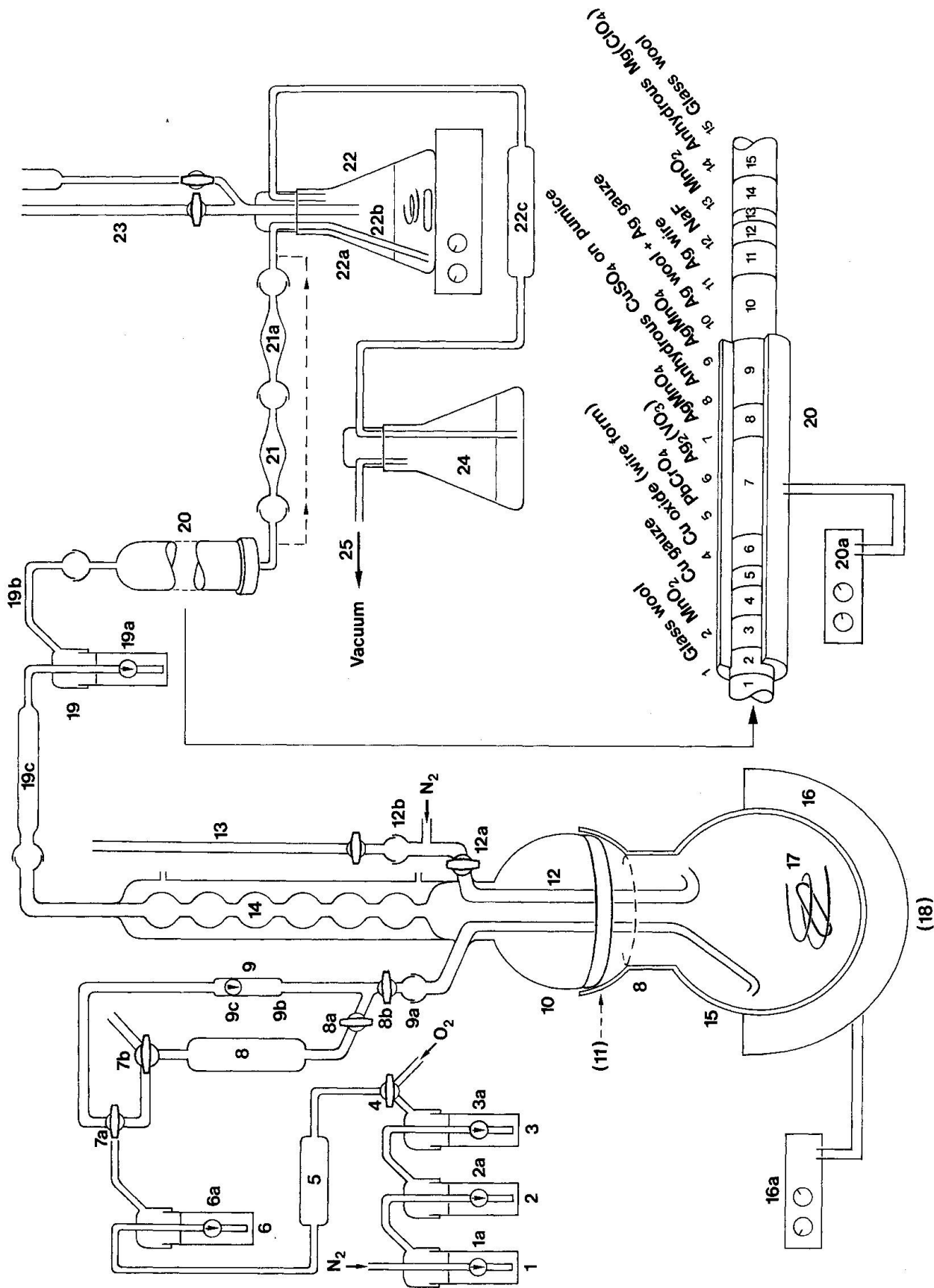
3. A gas wash bottle (250 ml) filled with Pyrogallol solution Merck (1 portion 25% Pyrogallol + 5 portions KOH 60%) may be used for the absorption of oxygen traces from the nitrogen. Alternatively a preheater consisting of a pyrex tube, containing analar reagent grade Cu foil, heated by heating cables and a regulator to about 500 °C for the absorption of O<sub>2</sub>, organic traces, S<sub>2</sub><sup>2)</sup>.
- 3a A non-return valve.
4. A three-way stopcock is also connected to oxygen-cylinder.
5. A guard tube, containing Na-Asbestos with indicator Merck, for the absorption of CO<sub>2</sub>.
6. A bubble counter, filled with concentrated H<sub>2</sub>SO<sub>4</sub> (saturated by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) to control the flow rate of N<sub>2</sub>.
- 6a A non-return valve.
7. A three-way stopcock.
- 7a A three-way stopcock.

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<sup>2)</sup> It may be replaced by a De-Ox (de-oxygenation catalyst Alfa, or BTS Fluka).

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- 1 Gas wash bottle (incl. H<sub>2</sub>SO<sub>4</sub> + CrO<sub>3</sub>)
- 2 Gas wash bottle (incl. Molecular sieve 5A or 13X)
- 3 Gas wash bottle (incl. Alkaline pyrogallol solution). It may be substituted by an other de-ox, such as acidic chromchloride solution.
- 1a, 2a, 3a non-return valves.
- 4 Three way stopcock
- 5 CO<sub>2</sub>-Absorption tube (incl. CO<sub>2</sub> absorber with indicator)
- 6 Bubble counter (incl. H<sub>2</sub>SO<sub>4</sub> + CrO<sub>3</sub>)
- 6a Non return valve
- 7a, b Three way stopcocks
- 8 Acid reservoir
- 8a, b Vacuum taps
- 9 Pyrex tube with Covar-glass connection
- 9a Spherical joint (ball and cup)
- 9b Pyrex tube (welded to the reflux condensor)
- 9c A check (non-return) valve
- 10 Spherical Cup
- (11 Adapter for the PTFE vessel)
- 12 Pyrex tube (welded to the reflux condensor)
- 12a Vacuum tap
- 12b Spherical joint (ball and cup)
- 13 Microburette for the titr. solution (e. g. KMnO<sub>4</sub>)
- 14 Reflux condensor
- 15 Disintegration vessel
- 16 Heating mantel for 15
- 16a Regel unit for 16
- 17 Magnetic stirrer
- (18 Lab-jack boy)
- 19 Gas wash bottle (incl. H<sub>2</sub>SO<sub>4</sub> + Ag<sub>2</sub>SO<sub>4</sub>)
- 19a Non return valve
- 19b Pyrex connection tube
- 19c H<sub>2</sub>O absorption tube (incl. P<sub>2</sub>O<sub>5</sub> on Pumice)
- 20 Long Pyrex absorption tube
- 20a Heating cable and regel unit
- 21 A Heating cable for 20 and regel unit
- 21,21a CO<sub>2</sub> absorption tubes (incl. CO<sub>2</sub> absorber with indicator)
- 22 Non-aqueous titration unit
- 22a Erlenmayer flask (filled with Dimethylformamide and Monoethanol amin)
- 22b Pyrex tube connection
- 22c CO<sub>2</sub>-Absorption tube (filled with Ascarite)
- 23 Microburette for the titr. CO<sub>2</sub> (filled with Tetrabutylammoniumhydroxide)
- 24 Erlenmayer flask (incl. H<sub>2</sub>SO<sub>4</sub> for the absorption of moisture from 25)
- 25 Water pump (Vacuum unit)

Disintegration Apparatus for the Analysis of CO<sub>2</sub> and FeO. (Legend see p. 98.)

## II. DISINTEGRATION UNIT

This consists of a compact upper part and a lower disintegration vessel (see fig. 1).

The upper part contains an acid reservoir and a reflux condenser, which are both welded to a spherical cup (55/45).

The individual parts of the upper unit are:

8. An acid reservoir, which consists of the two cylindrical separating funnels and pyrex tubes (1. ca. 50 ml; 2. 30 ml) includes a check valve, put together (see fig. 1).
  - 8a. The acid reservoir pyrex tube contains a standard ground socket and cone or quick fit connected with 7a. In the lower part, it has a O ring tap (8a), which controls the acid flow to the disintegration vessel (15).
  - 8b. O ring tap.
  9. The pyrex tube contains a hose connection, a non-return valve (check valve 9c).
  - 9a. Spherical connection (ball and cup joints): sealed with PTFE sleeves.
  - 9b. A pyrex tube connection with the disintegration vessel (15) is about 200 mm long and 5 mm in diameter and is welded to a reflux condenser and is connected with the acid reservoir and a spherical cup (10).
  10. A spherical cup joint.
  11. Connection piece from spherical cup to ground socket: it is used if the sample should be dissolved in a PTFE-disintegration flask.
  12. A pyrex tube connection to set a micro titration burette for the determination of FeO.
  - 12a O ring vacuum tap.
  - 12b Ball and cup joints.
  13. Microburette for FeO-titration.
  14. A reflux condenser, which is 600 mm long and is welded at the ends to a spherical cup joint (10).
- The lower part of the disintegration unit contains:
15. A rounded 250 ml flask, with a spherical ball joint, it is used as a disintegration vessel. According to the individual requirements it may be made of pyrex glass, or of quartz or of PTFE.
  16. A heating mantle is used for the heating of a rounded flask during the sample disintegration. It can be substituted for a bunsen burner.
  16. Regulation unit for the heating mantle.
  17. A magnetic stirrer is used to mix the solution in the sample disintegration.
  18. Lab-Jackboy: It is used to rise and set the magnetic stirrer.

The connection of I to II is by means of a PVC coupling, and the connection of II to III is performed by a pyrex tube, which is welded to the reflux condenser. The pyrex tube (19a), which is also welded to the long pyrex tube (20) is connected to the gas wash bottle (19) by means of spherical joints and fork clamps. The upper part of the disintegration unit (II) is fixed by clamps to the retort stand rools, whereas the lower part (disintegration vessel) is removeable.

## III. ABSORPTION UNIT

A gas wash bottle and a long pyrex tube (600 mm long, 15 mm in diameter) are used for the absorption of the components (except CO<sub>2</sub>) volatilized from the sample solution.

19. A gas wash bottle (200 ml), which contains concentrated H<sub>2</sub>SO<sub>4</sub> (saturated with Ag<sub>2</sub>SO<sub>4</sub>) absorbing H<sub>2</sub>O and halogens.
- 19a. Non return valve.
- 19b. A pyrex tube is welded to the long pyrex tube 20 and connected with spherical joints to the gas wash bottle (19).
20. A long pyrex absorption tube is filled for Ag<sub>2</sub>(VO<sub>3</sub>), MnO<sub>2</sub> + Ag<sub>2</sub>O, anhydrous CuSO<sub>4</sub> on Pumice, CuO, PbCrO<sub>4</sub>, Cu foil, CuO, Ag-wool, silver gauze, anhydrous Mg(ClO<sub>4</sub>) (see fig. 1), which are separated from each other by a layer of glass wool. It is heated to about 600 °C by heating cables between sections 2 and 10. It absorbs S and halogens components and traces of H<sub>2</sub>O.
- 20a. Heating cables and its control units.
21. The CO<sub>2</sub> absorption tube is a about 130 mm long pyrex tube, provided with spherical joints and filled with a mixture of soda asbestos (12–14 mesh) and anhydrous magnesium perchlorate.
- 21a. The CO<sub>2</sub> absorption control tube is used to control eventual losses of CO<sub>2</sub> escaping from the absorption tube (21) of CO<sub>2</sub>.
22. non-aqueous titration unit for the analysis of CO<sub>2</sub>.
- 22a. A 250 ml Erlenmeyer flash with standard ground socket 5 mm Ø filled with a Dimethylformamide + Monoethanolamine solution (absorbing CO<sub>2</sub>).
- 22b. A pyrex tube is melted to the standard ground cone and connected with the long pyrex absorption tube either by 21a or by 20 or directly (see fig. 1).
- 22c. A hose connection to CO<sub>2</sub>-absorbing tube (23).
- 22d. A microburette filled with Tetrabutylammonium hydroxide or potassium methoxide.
- 22e. Magnetic bar.
- 22f. Magnetic stirrer.
23. A CO<sub>2</sub>-absorption tube: it is used to prevent an introduce of CO<sub>2</sub> from the air.
24. A 500 Erlenmeyer flash with standard joint socket and cone. It is filled with concentrated H<sub>2</sub>SO<sub>4</sub> to prevent any moisture from the air. It is connected to a water pump (25).
25. A water pump provides a slight negative pressure at the end of the flow path and facilitates the gas flow.

## B. Reagents

N<sub>2</sub> is used as a carrier gas for CO<sub>2</sub> and produces a non-oxidizing environment in the apparatus.

*For the dissolution of the sample the following reagents are used*

|                                |          |                            |
|--------------------------------|----------|----------------------------|
| HF                             | (40%)    | p.a. (Merck or equivalent) |
| H <sub>2</sub> SO <sub>4</sub> | (96–98%) | p.a. (Merck or equivalent) |
| H <sub>3</sub> PO <sub>4</sub> | (85%)    | p.a. (Merck or equivalent) |
| HNO <sub>3</sub>               | (65%)    | p.a. (Merck or equivalent) |

*For the absorption of H<sub>2</sub>O*

Mg-perchlorate p.a. (Merck or equivalent)  
 Sicapent p.a. (Merck)  
 H<sub>2</sub>SO<sub>4</sub> p.a. (Merck or equivalent)  
 P<sub>2</sub>O<sub>5</sub> (on Pumice) p.a. (Merck or equivalent)

*For the analysis of CO<sub>2</sub>*

Ascarite (8–20) anal R. A.H.T.  
 0.02 N tetrabutylammonium hydroxide in toluene (Fluka) or potassium methoxide (BDH)  
 Na-asbestos with indicator Merck.  
 Dimethylformamide + monoethanolamine as indicator 0.1% thymolphthalein p.a. Merck.

For the absorption of SO<sub>2</sub>, H<sub>2</sub>S, S, O<sub>2</sub> and halogens, the following reagents are used:

- 1) Ag<sub>2</sub>(VO<sub>3</sub>) p.a. (Merck or equivalent)
- 2) Ag<sub>2</sub>O + KMnO<sub>4</sub> p.a. (Merck or equivalent)
- 3) Ag-wool p.a. (Merck or equivalent)
- 4) Anhydrous CuSO<sub>4</sub> (on Pumice) p.a. Merck or equivalent
- 5) Cu-gauze
- 6) CuO in wireform p.a. Merck
- 7) PbCrO<sub>4</sub> p.a. Merck
- 8) Glass wool p.a. Merck
- 9) Silversulfat p.a. Merck or equivalent
- 10) MnO<sub>2</sub> p.a. Merck or equivalent

Pyrogallol solution 25% (1 portion Pyrogallol + 5 portions KOH 60%) p.a. Merck.

The aluminium foil (anal R.) serves to weigh the sample and to prevent the volatilization of the excess fluorine from the solutions (F is bound to Al forming a stable Al-fluorine complex).

*For the determination of FeO*

KMnO<sub>4</sub> p.a. Merck: 0.1 N titrisole ampule diluted to 0.02 N  
 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> p.a. Merck: 0.1 N titrisole ampule diluted to 0.02 N

**C-Disintegration of the Sample**

Accurately weigh 0.3–1.5 g of sample on a piece of aluminium foil (e.g. 0.1 mm thick, 50 × 30 mm wide) and close the sample by folding the foil tight. Remove the disintegration vessel (15) from the disintegration unit (II). Put the foil with the sample into the vessel. Add a magnetic bar and 10–20 ml cold H<sub>2</sub>O (boild immediately before). Set again the disintegration vessel in its place, fix the clamps. Then put the heating mantle (16) and the magnetic stirrer (17) on a lab-jack under the disintegration vessel.

Turn off the tap 8a and close the way to 7b by means of three way stopcock (7a). Put 15–25 ml H<sub>3</sub>PO<sub>4</sub> + 1–2 ml H<sub>2</sub>SO<sub>4</sub> in to the acid reservoir (8) by means of the outlet of 7b.

Turn on the valves of the N<sub>2</sub>-cylinder and water pump (25). During the passing of N<sub>2</sub> through check valve (9) and in the apparatus (1–25) the air is removed continuously.

After 15–20 minutes the CO<sub>2</sub>-absorption tubes (21, 21a) are removed from the system and weighed accurately. It is put again on the apparatus. Turn off the taps 8b and turn on 7b and 8a. Now N<sub>2</sub> is passing through the acid reservoir and goes out to the air. The traces of the air in the acid and the acid reservoir (8) are also removed by N<sub>2</sub> in a few minutes.

Open the way to 7b by means of the three way stopcock (7a) and close the way to the outlet at 7b by means of the three way stopcock. Turn on the taps 8a and 8b.

The acid is removed completely from the acid reservoir (8) by means of N<sub>2</sub> to the disintegration vessel (15). The taps 7b and 8a are closed. During the disintegration procedure N<sub>2</sub> is passed through check valve (9). It is a non-return valve. Start the control unit (20a) for the heating of the long absorption tube (20), and the control unit (16a) for the heating mantle (16) and also magnetic stirrer (17).

The sample is dissolved by heating at about 180 °C under a continuous nitrogen current. The nitrogen flow rate is continuously controlled during the dissolution procedure. The dissolution procedure is continued until the Al foil disappears completely. Then the solution is heated for a further 3–5 minutes at about 100 °C. The control unit of the heating mantle is turned off. 30 ml of cold previously boiled H<sub>2</sub>O and ca. 2.5 ml HF (40%) are added to the acid reservoir by means of 7b.

The glass is only slightly attacked by could diluted HF. The reagent is moved slowly by means of taps (8a und 8b) and nitrogen to the disintegration vessel (15). After adding and vigorously stirring the solution, the precipitates would be dissolved completely. For the removal of any excess of fluorine, the solution is heated for 2–3 minutes at about 60–70 °C. An additional 50 ml H<sub>2</sub>O is added and mixed well with the contents of the vessel.

## D. Determination of CO<sub>2</sub> and FeO

### 1. DETERMINATION OF INORGANIC CARBON

The CO<sub>2</sub> (inorganic carbon), which is evolved during the disintegration of the sample by HF + H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub> is absorbed in a Na asbestos + magnesium perchlorate absorber and determined gravimetrically: Disconnect 21a from 22; detach 21 from 21a. Remove the absorption tube 21 from the long pyrex tube (20). Weigh 21 and 21a, separately and obtain the increase in weight (= CO<sub>2</sub>). If there is no loss of CO<sub>2</sub>, the first absorption tube (21) contains all the CO<sub>2</sub> evolved. The non-aqueous titration unit (22) is an additional control and is used to check the loss of CO<sub>2</sub>, which could not be absorbed by means of CO<sub>2</sub>-absorption tubes (21 and 21a). This unit can be connected with a long pyrex tube (21) without difficulties for the titrimetric analyzing of CO<sub>2</sub> by means of

non-aqueous titration, which is recommended by several analysts (e.g. Read 1972, Sen Gupta 1970). The determination of total carbon cannot be carried out before the determination of ferrous iron.

## 2. DETERMINATION OF FERROUS IRON

The ferrous iron determination can be carried out colorimetrically or volumetrically (e.g. AYRANCI, 1976; RILEY et al., 1959; SEIL, 1943; Wilson, 1960).

### a. Colorimetric determination:

Transfer the sample solution immediately and quantitatively from the disintegration vessel (15) to a conical flask (200 ml) and dilute with cold boiled  $H_2O$  to the mark. Pipette a suitable aliquot (3–5 ml) of the solution to a volumetric flask (100 ml). Add the reagents and measure the absorbance of the colored solution against a blank of a standard in solution (see AYRANCI, 1976). The total iron can also be determined in a further portion of solution after reduction of ferric iron by means of a suitable reducing agent (e.g. hydroxylaminhydrochloride).

### b. Volumetric determination:

If the sample solution has to be used to determine ferrous iron and  $CO_2$ , the volumetric determination is performed in the disintegration vessel after the evolution of inorganic carbon.

Fill a burette (e.g. 25 ml with 0.02 ml graduated divisions and a straight stop-cock) with 0.1 N  $KMnO_4$  (or 0.1 N  $Ce(SO_4)_2$  or 0.1 N  $K_2Cr_2O_7$ ) solution; 0.02 N  $KMnO_4$  standard solution is recommended especially for the determination of low iron concentration. Set on the burette to the conical (12b) and turn on the tap (12a). Start the magnetic stirrer (17). Run 0.1 or 0.02 N  $KMnO_4$  standard solution into the sample solution dropwise from the burette until the sample solution in the disintegration vessel turns faintly pink.

Calculate the FeO concentration

1 ml 0.1 N  $KMnO_4 \triangleq 7.185$  mg FeO.

In the determination of ferrous iron by means of 0.1 or 0.02 N  $K_2Cr_2O_7$  and  $Ce(SO_4)_2$  standard solution, the endpoint is detected by diphenylamine (2–3 drops 0.2% aqueous solution of barium diphenylamin sulfonate) or ferroin (1–2 drops) indicators.

## 3. DETERMINATION OF TOTAL $CO_2$

The determination of total carbon is carried out subsequent to the analysis of ferrous iron as follows:

Remove the burette from the standard ground socket and add 2–3 ml of an oxidizing acid (e.g. HNO<sub>3</sub>, H<sub>2</sub>CrO<sub>4</sub>). Turn off the tap (12b). Run the O<sub>2</sub> current by means of three-way stopcock (4) and boil briefly the solution to destroy any organic impurities (e.g. graphite). Again weigh the CO<sub>2</sub> absorption tubes (21 and 21a); calculate the total CO<sub>2</sub> from the weight increase of the CO<sub>2</sub> absorbers.

#### 4. DETERMINATION OF TOTAL IRON (= as FeO)

For the volumetric determination of total iron, the sample solution in the disintegration vessel, which was used before in the titration of ferrous iron, may be used again. For this purpose, the total ferric iron is reduced by means of a reducing agent (e.g. SnCl<sub>2</sub> solution) to the ferrous state. The titration is carried out with KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> etc. standard solutions.

The analytical procedure is reported in text books (e.g. MAXWELL, 1968, p. 422).

#### E. Conclusions

The apparatus (see fig. 1), which is used for the disintegration of the sample and for the simultaneous routine analysis of CO<sub>2</sub> and FeO, is made in accordance with microanalytical determination techniques for CO<sub>2</sub> and H<sub>2</sub>O analysis (e.g. RILEY et al., 1959; MEYROWITZ, 1970). Nevertheless it is used usually for routine macroanalysis. The sample is dissolved by means of a mixed acid (diluted HF + H<sub>2</sub>SO<sub>4</sub> + H<sub>3</sub>PO<sub>4</sub>), which is generally known as a powerful and non-oxidizing solvent. It can be used for the disintegration of carbonates and silicates. The sample dissolution procedure is performed in a non-oxidizing environment of N<sub>2</sub>, so that the condition is suitable for the analysis of inorganic carbon and ferrous iron.

In the dissolution of the sample with H<sub>3</sub>PO<sub>4</sub> and HF, stable and colorless complexes of Fe(III) are formed such as [Fe(PO<sub>4</sub>)<sub>2</sub>]<sup>3-</sup> and eventually some [FeF<sub>6</sub>]<sup>3-</sup>. Hence the formal oxidation/reduction potential of this system is therefore more suitable for the oxidimetric titration of ferrous iron. Normally FeO is titrated with a 0.1 or 0.02 N standard KMnO<sub>4</sub> solution and by visual end point determination.

Incorrect values of FeO may also result from the disintegration procedure (of the sample): Incomplete dissolution of sample and oxidation (especially Fe(II) to Fe(III) in the solution or vice versa prior to determination.

The disintegration apparatus (see fig. 1) is suitable for the purpose envisaged:



The complete dissolution of the sample can be controlled very easily. If necessary, additional acids can be added without removing the  $N_2$ -flow during the prolonged heating. The determination of ferrous iron can be carried out in the same disintegration vessel. The determination of total carbon, inorganic carbon and total iron can be performed during the same analytical procedure and from the same sample.

The disintegration vessel and apparatus can be used for the dissolution of fusion cakes. If the disintegration glass vessel is replaced by a PTFE vessel and the determination of FeO and total Fe not carried out in the apparatus, it is possible to analyze additional components.

The standard ground cone of disintegration vessel (15) has a wide aperture, so that a crucible (about 25 ml) can be introduced without difficulty into the disintegration vessel. Thus the sample can be disintegrated in the crucible under a continuous current of  $N_2$ . If, for the disintegration of the sample by means of flux a higher temperature ( $\sim 1000^\circ C$ ) is needed, the glass vessel (15) has to be replaced by a quartz vessel. The sample may be decomposed by a non-oxidizing flux (e.g.  $B_2O_3$ ,  $LiBO_2$ ) under  $N_2$  flow. The fusion product (cake) can be dissolved by a non-oxidizing acid within the same disintegration vessel (15). Using such a procedure it is also possible to determine ferrous iron in the sample solution (see AYRANCI, 1976; further details will be reported in a forthcoming paper). According to the above cited discussion, it can be seen that the disintegration apparatus may be used for various purposes:

- 1) For the wet-disintegration procedure; for the disintegration by flux,
- 2) for the dissolution of fusion cakes,
- 3) as a combustion apparatus for the analysis of  $H_2O$  and  $CO_2$ . For this purpose it is only necessary to remove the gas wash bottle (19) and to remove  $H_2O$  absorber end of the long pyrex tube (20). Then the reflux condenser (14) is connected with long pyrex tube (20). They are heated to about  $600^\circ C$  by means of a heating cable.

$H_2O$  is absorbed by a  $H_2O$  absorber (e.g. sicapent) in a tube (21), which is fitted at the one end to the long pyrex tube (20) and at the other end to the  $CO_2$  absorber (21 a).

In the following table (1) the analytical results of the  $CO_2$  and FeO determinations in various samples are given. The analysis have been carried out by means of above illustrated apparatus, using an acid disintegration procedure.

The analytical results reveal that the proposed procedure in fact can be used for the determination of carbonate and silicate samples.

The estimated errors of mean values range within  $\pm 0.3\%$  for  $CO_2$  and  $\pm 0.4\%$  for FeO, if a sample weight of approximately 300 mg is used.

Table 1 Analytical results of CO<sub>2</sub> and FeO\* determinations of the selected samples.

| Sample                               | Weight of sample used in analysis mg | Number of determinations            | CO <sub>2</sub> |       | Weight % Number of determination | FeO  |       |
|--------------------------------------|--------------------------------------|-------------------------------------|-----------------|-------|----------------------------------|------|-------|
|                                      |                                      |                                     | a               | b     |                                  | a    | b     |
| Ca CO <sub>3</sub> p.a.<br>99% MERCK | 100-300                              | 44.1; 43.85; 43.95; 44.05;<br>44.15 | 44.02           | 43.97 | nd                               | -    | 0.001 |
| Limestone<br>ZGI-KH                  | 150-250                              | 37.65; 37.8; 37.75; 37.6            | 37.70           | 37.60 | nd                               | -    | 0.34  |
| Slate<br>ZGI-TB                      | 400-1000                             | 0.15; 0.1; 0.15                     | 0.13            | 0.13  | 5.5; 5.4; 5.35                   | 5.4  | 5.43  |
| Basalt<br>GSJ-JB-1                   | 600-1000                             | 0.2; 0.15; 0.15                     | 0.18            | 0.19  | 6.0; 6.1; 5.9                    | 6.0  | 6.06  |
| Basalt<br>CRPG-BR                    | 250-400                              | 0.8; 0.85; 0.75                     | 0.8             | 0.86  | 6.7; 6.6; 6.65                   | 6.65 | 6.57  |
| Basalt<br>ZGI-BM                     | 400-600                              | 1.3; 1.4; 1.35; 1.4                 | 1.4             | 1.34  | 7.3; 7.35; 7.30; 7.35            | 7.30 | 7.28  |
| MgCO <sub>3</sub><br>Lab. Stand.     | 100-300                              | 52.1; 52.1; 51.9                    | 52.05           | 52.2  | nd                               | nd   | nd    |
| Diorite<br>ANRT-DR-N                 | 500-800                              | 0.1; 0.12                           | 0.1             | 0.13  | 5.4; 5.35                        | 5.4  | 5.42  |

## Abbreviations:

a) Mean values resulting from several determinations according to the proposed procedure.

b) Calculated or recommended values. - References (e.g. FLANAGAN, 1973).

\*) Volumetric determination by means of 0.02 N KMnO<sub>4</sub>-standard solution.  
n.d. not determined.

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