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Simultaneous Determination of Inorganic-, Total-CO₂ and H₂O in routine Rock Analysis

by *B. Ayranci**

Abstract

A routine rapid analytical method is presented for the simultaneous determination of the inorganic-, total-CO₂ and H₂O components of geological samples. The apparatus used in this procedure is a combination of acid attack and combustion train methods, which are coupled to each other.

At the end of the sample disintegration the analysis of components may be carried out, according to the equipment in the laboratory, by means of a selected method (e.g. gravimetrically, volumetrically gas-chromatographical, IR-absorption procedures).

The automatic determination of many components of a rock has so far not been accomplished by means of only one of the known analytical methods and modern instruments (such as AAS, ICP, NAA, XRF). This is due to the analytical problems, which vary depending upon the components to be analysed in the sample. For example: The analysis of ferrous and ferric iron or SO₃, SO₄, H₂O, CO₂ can not be carried out either by XRF or NAA or AAS. However, the total iron (as Fe₂O₃) is analysed successfully by means of these methods. Furthermore these instruments are very useful for serial analysis of many components of a rock. Because the determination of the concentrations of several components (e.g. F, Cl, B, SO₄, CO₂, H₂O, As₂O₃) requires individual methods (e.g. colorimetric, volumetric, gravimetric procedures) such elements are commonly analysed separately. Therefore any analytical technique, which can determine several components by the same procedure simultaneously is of great advantage to analysts (as is often done in organic elemental CHN automatic determinations).

This work discusses the possibility of a simultaneous routine analysis of inorganic-, total-CO₂, and H₂O of the rock samples. The analytical methods commonly used to determine inorganic and total CO₂ and H₂O in the rock samples require two independent procedures:

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1. The analysis of (inorganic-, organic-, total-) CO₂ is carried out after an acid treatment of the sample.
2. The recovery of total CO₂ and H₂O is performed by means of pyrolysis of the sample in a combustion technique.

For the determination of inorganic CO₂, the sample is dissolved by means of non-oxidizing acids. The organic and total CO₂ analysis are carried out by means of an oxidizing acid attack. The total CO₂ can also be calculated after the recovery of inorganic-, and organic CO₂ in succession; at first the inorganic CO₂ is recovered (after dissolving the sample by none oxidizing acids) and then the organic CO₂ is determined after adding a suitable agent (e.g. CrO₃) to the sample solution.

One of the great advantages of this procedure is the estimation of the ferrous and total iron concentration of the sample solution during the analysis (AYRANCI, 1979; BOUVIER et al., 1972).

The combustion technique, which is commonly used for the determination of the total CO₂ concentration also enables the simultaneous analysis of H₂O (GEL'MAN et al., 1968, RILEY et al., 1959); but the analysis of the inorganic and organic CO₂ of the sample by means of combustion train are complicated. The advantages of the pyrolysis method is to estimate several additional components (e.g. S, N, Cl,) which are also liberated during the pyrolysis of the sample (e.g. KOZLOWSKI and NAMIESNIK, 1979, MAZUREK-KOBYLINSKA, et. al., 1979).

The inorganic-, organic-, total-CO₂ and H₂O, furthermore the ferrous and total iron components of a sample may be analysed simultaneously, if an acid attack procedure (used for the recovering of CO₂ and FeO, AYRANCI, 1978) is coupled with a combustion technique (see fig. 1). For the analysis of the above cited components it is necessary to weigh two sample aliquots: One of the sample portion is put into the disintegration vessel (3) and the other portion is used in pyrolysis section (II-c) of the apparatus. The acid attack and the combustion procedures of the aliquots are carried out simultaneously during the analysis of the sample.

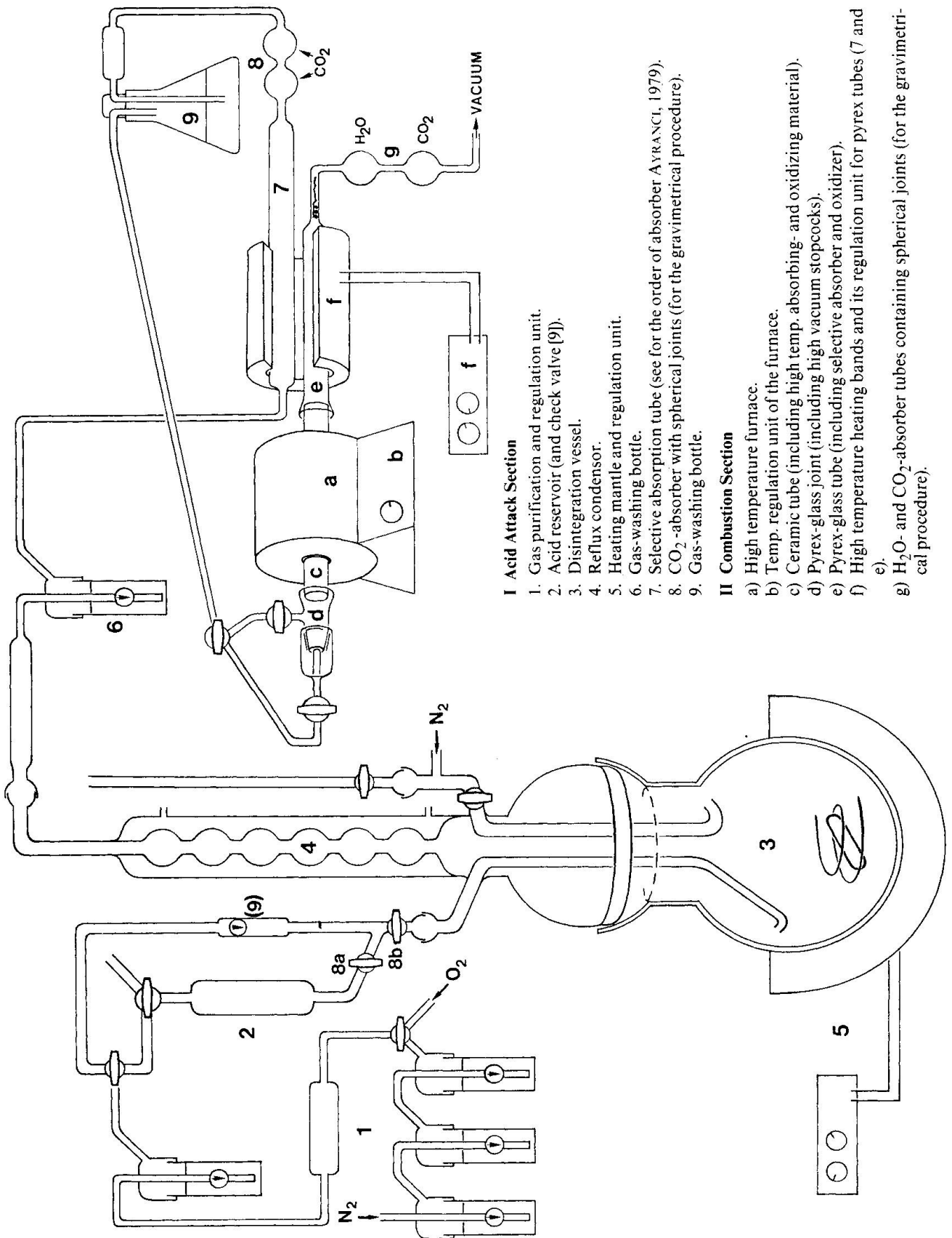
The inorganic-, organic-, total-CO₂ and the ferrous and total iron are recovered from the acid treatment, the total CO₂ and H₂O are estimated from the combustion train. The apparatus may also be used for only one of the two procedures, if required.

ANALYTICAL PROCEDURE

A - Apparatus

The apparatus necessary for this analytical procedure utilizes a combination of an acid attack procedure (which was previously used to recover CO₂ and

Fig. 1: A coupled acid attack and combustion train apparatus used for the simultaneous disintegration of sample aliquots by acids and pyrolysis procedures.



I Acid Attack Section

1. Gas purification and regulation unit.
2. Acid reservoir (and check valve [9]).
3. Disintegration vessel.
4. Reflux condenser.
5. Heating mantle and regulation unit.
6. Gas-washing bottle.
7. Selective absorber tube (see for the order of absorber AYRANCI, 1979).
8. CO₂-absorber with spherical joints (for the gravimetric procedure).
9. Gas-washing bottle.

II Combustion Section

- a) High temperature furnace.
- b) Temp. regulation unit of the furnace.
- c) Ceramic tube (including high temp. absorbing- and oxidizing material).
- d) Pyrex-glass joint (including high vacuum stopcocks).
- e) Pyrex-glass tube (including selective absorber and oxidizer).
- f) High temperature heating bands and its regulation unit for pyrex tubes (7 and e).
- g) H₂O- and CO₂-absorber tubes containing spherical joints (for the gravimetric procedure).

FeO, AYRANCI, 1978) and a combustion technique (fig. 1). It may also be considered as two independent trains put together for the absorption of the unfavourable components evolving during the decomposition of aliquots of a sample.

I - The acid Attack Section

This part has been reported in detail in an earlier paper (AYRANCI, 1979) and it is summarized here:

1. A gas purification and regulation unit of a carrier gas.
2. An acid reservoir, which is filled with acids, used for the dissolution of the sample and connected with the disintegration vessel (3) by welding to the cup a, spherical joint.
3. A rounded (glass or PTFE) flask, is used as disintegration vessel.
4. A reflux condensor, which is welded (as the 2) to the cup of disintegration vessel (3) and to a gas washing bottle (6). It is used to recover the H₂O volatilizing from the sample solution during the disintegration procedure.
5. The heating mantle and the temperature regulation unit, which is necessary to heat the disintegration vessel for the dissolving of the sample.
6. A gas washing bottle, filled with H₂SO₄ (saturated by Ag₂SO₄). It absorbs the moisture of gases and eliminates S-components evolved during the sample decomposition.
7. A long pyrex tube (selective absorption tube). It is ca. 500 mm long and its diameter ca. 20 mm and filled with suitable absorbers and used with the gas washing bottle (6) for the elimination of the unfavourable components, which adversely affect the analysis of CO₂ (e.g. H₂O, SO₂, H₂S, Cl, F, SiF₄, H₂SiF₆).
8. The absorption and recovery unit for CO₂ (e.g. volumetrical, gravimetrical supply).
9. A gas washing bottle, which contains concentrated H₂SO₄ and a guard tube (filled with ascarite). It is used to collect the carrier gas and connected with the combustion section by PVC coupling.

II - The Combustion Section

It consists of the following units:

- a. A tabular high temperature furnace (Hereaus). It is ca. 450 mm long, its diameter is ca. 30 mm and may be heated at the middle zone up to 1500 °C.
- b. The temperature regulation unit of the furnace.

- c. A high quality ceramic tube (Alsinit, Haldenwanger Al₂O₃ 99.8%). This is about 650 mm long, its diameter is ca. 28 mm and open at both ends.
- d. The pyrex-glass joint. It is passed by a flat flange over the ceramic tube and tightened by a special O-ring gasket (Calrez, Dupont). The packing shows no leakage to about 10⁻⁵ mm Hg. The pyrex joint has at the other end a standard cone and is closed by a standard socket, which is welded to a high vacuum stopcock. A second high vacuum stopcock is also welded to the standard cone at the side.
- e. A long pyrex tube (selective absorption tube). It is also passed by flat flange over the ceramic tube and tightened by calrez O-ring. It is about 450 mm long and its diameter ca. 18 mm. It is filled with absorbers used for the elimination of the undesirable components disturbing the analysis of CO₂ and H₂O (e.g. Cl, F, H₂S, SO₂, H₂SiF₆). Both absorption tubes (7 of the acid attack and e of the combustion sections) are put together and coupled, so that they can be heated by using the same heating band during the analytical procedure.
- f. The heating band unit. It is a high temperature (Hereaus) band used to heat pyrex tubes (7 and e) for the quantitative and selective absorption of the unfavourable components evolving during the pyrolysis of sample with CO₂ and H₂O. The heating band may be regulated (by Herastat) up to 900 °C at given temperatures automatically.
- g. The absorption and recovery units for CO₂ and H₂O (e.g. gravimetical, volumetrical supply).

B - The Selection and The Packing of Absorbers

Several components (e.g. F, Cl, SO₂, SiF₄, Hg, H₂S, H₂SiF₆) which affect the analysis of CO₂ and H₂O adversely are eliminated by means of suitable absorbers, which are known in analytical chemistry. The packing of absorber, which are used for acid attack and combustion trains is slightly different, but the order of the absorbing materials in pyrex tubes (7 and e) is quite similar. However, the absorber used to eliminate the traces of H₂O in combustion section is obviously absent. In the combustion train, some of the materials, which may be used more efficiently at higher temperatures (e.g. Pt-Asbestos, Pt-gauze set as catalisator, MgO, CeO₂/La₂O₃ as efficient absorber for F, H₂SiF₆, As, P and CuO, Co₃O₄ as oxidizer) are put just after the Pt-, or ceramic -boat (containing the sample aliquot) in to the ceramic tube.

The order of the packing of absorbing materials used in acid attack and combustion sections of the apparatus may be summarized as follows:

B-1 The absorbing material and the contact zone used for acid attack section (it is ordered from the reflux condensor to the detection unit of CO_2):

- i) H_2SO_4 (saturated with Ag_2SO_4)
- ii) P_2O_5 (on pumice)
- iii) Absorbing and oxidation contact material in the long pyrex tube

- | | |
|--|---|
| 1) Quartzwool | 11) AgMnO_4 |
| 2) Cu-gauze | 12) Ag-wireform |
| 3) CuO-wireform | 13) Ag-wool |
| 4) Cu-gauze | 14) AgMnO_4 |
| 5) CuO-wireform | 15) Ag-wool |
| 6) PbCrO_4 | 16) NaF |
| 7) $\text{Ag}_2(\text{VO}_3)$ | 17) MnO_2 |
| 8) CuSO_4 (Anhydrous on pumice) | 18) $\text{Mg}(\text{ClO}_4)$ anhydrous |
| 9) Ag-wool | 19) MnO_2 |
| 10) Ag_2O | 20) Quartzwool |

The absorbers used in the pyrex tube are separated from each other by a layer of quartzwool. The traces of H_2O and the SO_2 are mainly absorbed at the first section (i, ii). The second part of the packing (iii, the material in the pyrex tube) allows the elimination of halogens and S-components, H_2O , H_2SiF_6 . The oxidation of C and CO to CO_2 and the reduction of nitrogen oxides to N_2 also occur in the same section (iii). The pyrex tube is heated between the section 2-14 to about 600°C for the activation of contact material by means of heating band.

B-2 The packing of the absorbers used in the combustion section is arranged in the following sequence:

- i) A zone of high temperature materials (from 1000°C to 750°C) Pt-asbestos + Pt-gauze as a catalizer; MgO , $\text{CeO}_2/\text{La}_2\text{O}_3$; CuO , Co_3O_4 (as absorbers and oxidizer).
It is used to remove some undesirable components (such as F, SiF_4 , As, P) and facilitates the oxidation of C, CO to CO_2 and H_2 to H_2O during pyrolysis of the sample and transport of gases. These high temperature efficient materials set after the sample (in Pt-, or ceramic-boat) and Pt-asbestos + Pt-gauze into the ceramic tube.
- ii) The absorbing and oxidation contact material used in the long pyrex tube (e): The packing order and the sort of material is the same as in the pyrex tube of the acid attack section (see above). The anhydrous magnesium perchlorate is obviously removed and a piece of silver

wire is extended to the end of pyrex tube to prevent condensation of H₂O. Furthermore a piece of gold wool is added to the packing of absorbers for the elimination of Hg-traces, if they evolve from the sample. The selection and the ordering of absorbers required in the apparatus is carried out according to the methods of micro-analytical technique, which was also discussed in detail by EHRENBERGER und GORBACH (1973). The inert carrier gas, which is regenerated after leaving the acid attack section, is transferred by a coupling between the gas washing bottle (9) and the high vacuum stopcock of the pyrex glass joint to the combustion train. Hence, an additional purified carrier gas and a regulation unit for the combustion train is not needed. However, a supplementary gas inlet may be necessary (if any T-shape connection is present before inlet of gases) for a short time in the pyrex glass joint in order to prevent the introduction of air during the placing of the sample into the combustion tube.

The wrapping of the heating band, used for the simultaneously heating of both pyrex selective absorbing tubes (7 and e), is extended on the pyrex tube e, so that the condensation of H₂O evolving during pyrolysis of the sample may be prevented.

C - Disintegration of Sample

Two sample aliquots are accurately weighed over a piece of aluminium foil and placed into the Pt-, or ceramic-boat. The aliquot used for the disintegration by acid attack is sealed by carefully folding the aluminium foil and placing it in the disintegration vessel (3).

The lab. jackboy and the heating mantle of the vessel (5) are lifted up and the vessel is moved from the cup of spherical joint. The sample (sealed in the foil) is transferred with a magnetic bar into the vessel and it is fixed again to the cup of the joint. Then the heating mantle is carefully placed under the vessel and fixed. The magnetic stirrer is elevated up to the heating mantle by means of the lab. jack-boy. The regulation unit of the heating band for the pyrex tubes is started to initiate the activation of the absorber. N₂ is introduced, and with the continuous inflow of nitrogen the air is expelled from the apparatus. The acid reservoir of the acid attack section is filled with a non-oxidizing diluted acid (e.g. 30-40 ml H₂SO₄ + H₃PO₄). Air from the acid reservoir (2) is removed after turning off the high vacuum stopcock (8b in fig. 1) by means of a nitrogen current, the procedure, for which has been reported in detail (AYRANCI, 1979). The nitrogen, passing through the combustion section due to the closed circulation, also continuously removes air from the ceramic-, pyrex-tubes and from the absorber used for recovering CO₂ and H₂O.

During the flow of N_2 via the side stopcock of the pyrex glass joint, the ground socket is removed from the ground cone. The aliquot of sample present in the Pt-, or ceramic-boat is gradually pushed into the heated zone of the ceramic tube. Before the beginning of disintegration procedures, the apparatus is rinsed out once more by increasing the nitrogen current for about 10-15 minutes.

The absorption tubes used for the gravimetical analysis of inorganic (+ organic) CO_2 derived from the acid attack, and total CO_2 and H_2O from the combustion sections are detached easily by means of spherical joints, and weighed accurately. Then they are attached again to the long pyrex tubes, containing conical balls. The acid, needed to dissolve the sample (present in aluminium foil) is moved into the disintegration vessel by means of the nitrogen current, after turning on stopcocks (8a, 8b). The stopcock 8a is turned off and the nitrogen passed only through the check valve (9) during the decomposition procedure. Taps of water are turned on to allow cold water circulation in the reflux condenser and in the vacuum unit. Regulation units of the heating mantle the magnetic stirrer and the combustion furnace are started for the acid treatment and for pyrolysis of the sample aliquots. The temperature of the heating mantle is elevated for few minutes to about $200^\circ C$ and then gradually reduced over 20 minutes to $180^\circ C$ and then to $40^\circ C$ over another 20 minutes. Then 10-15 ml of previously boiled cold H_2O and 1-2 ml HF (40%) are added to the sample solution and heated again to about $70-80^\circ C$ for a short time. The disintegration procedure is completed after the appearance of a clear solution. This sample solution may be used in the analysis of ferrous iron by several methods (e.g. colorimetrically or volumetrically by $KMnO_4$, $K_2Cr_2O_7$, $C(SO_4)_2$).

The CO_2 , evolving in the course of acid attack disintegration is carried out continuously by means of nitrogen current, and is separated from the other components selectively, passed through absorbers. In the combustion section, the temperature of furnace is increased to about $1200-1300^\circ C$ for pyrolyzing the sample. The volatile components, (including total CO_2 and H_2O) evolving during the decomposition of sample are rinsed out for the selective absorption of components by means of a nitrogen current, which was regenerated after the outlet of the acid attack section.

D - Determination of Components

The inorganic CO_2 (evolved from the acid attack procedure of sample) and the total CO_2 and H_2O (liberated by means of prolysis of sample) are estimated commonly by gravimetical method. The absorption tube used to recover CO_2 includes natron asbestos (with indicator) and the H_2O absorber consists of P_2O_5 (on pumice), anhydrous $CaCl_2$ or $Mg(ClO_4)_2$. The H_2O and CO_2 can be also ab-

Tab. 1: Analytical results of several rock standards recovered simultaneously by means of a coupled acid attack and combustion disintegration procedure.

Sample	Combustion Section		Recovered total		Acid Attack Section		Recovered Inorganic CO ₂ %		Recommended total		References
	Weight of aliquots used in analysis (gr)	H ₂ O %	CO ₂ %	Weight of aliquots used in analysis (gr)	Inorganic CO ₂ %	H ₂ O %	CO ₂ %	H ₂ O %	CO ₂ %		
USGS-SCo-1 Shale	0.200	6.2	3.4	0.200	2.6	6.3	2.65	6.3	2.55+(0.18)**	FLANAGAN (1976) USGS Prof. Paper 840 "	
	0.500	6.35	3.55	0.300	2.5	(3.85+2.45)*	2.65	(3.85+2.45)*			
USGS-MAG-1 Marine Mud	0.100	8.15	6.1	0.300	0.65	7.8	0.6	7.8	0.51+(1.43)**	"	
	0.200	8.05	6.4	1.0	0.65	(5.22+2.58)*	0.6	(5.22+2.58)*			
GSJ-JB-1 Basalt	0.250	2.05	0.24	0.200	0.2	1.98	0.2	1.98	0.19	ABBEY (1972) FLANAGAN(1973) (s.literature)	
	0.400	2.05	0.24	0.400	0.2	(1.0+0.98)*	0.2	(1.0+0.98)*			
CRPG-BR Basalt	0.300	2.85	1.0	0.300	0.8	2.80	0.85	2.80	0.9	ABBEY (1972) M. ROUBAULT et al. (1970) Sci.de la Terra Nancy	
	0.400	2.7	0.95	0.400	0.8	(2.30+0.5)* 2.60 (2.30+0.30)*	0.85	(2.30+0.5)* 2.60 (2.30+0.30)*			
**** ZGI-BM Basalt	0.200	3.75	1.45	0.100	1.4	3.62	1.45	3.62	1.34	FLANAGAN (1973)	
	0.300	3.70	1.30	0.350	1.4	3.62	1.45	3.62			
**** ZGI-KH Limestone	0.100	1.1	37.9	0.05	37.4	1.0	37.55	1.0	37.6	"	
	0.150	1.05	37.8	0.100	37.8	1.0	37.55	1.0			
**** SSC-MRG-1 Gabbro	0.400	1.08	1.15	0.500	1.0	1.02	1.05	1.02	1.04	ABBEY et al. (1975) Canmet, Montreal	
	0.500	1.05	1.10	0.300	1.08	1.02	1.05	1.02			

Abbreviations:

- * H₂O
- ** organic C
- *** H₂O⁺
- **** moisture free basis aliquots

sorbed during combustion or acid attack section by means of special absorbers (e.g. molecular sieve 5A or 13X) simultaneously and then can be liberated again by heating during the volumetrical analysis (e.g. coulometrical, non-aqueous or Karl-Fischer titration methods). Alternatively analysis may be carried out by using automated instruments (such as gas-chromatographical, IR absorption methods), if available.

CONCLUSION

The analytical procedure described in this work enables the simultaneous recovery of inorganic-, total CO_2 and H_2O components of geological samples during the wet-chemical routine analysis.

The procedure may be extended for the estimation of ferrous, total iron and the organic CO_2 components of a sample. One of the important problems for the determination of ferrous iron during the analytical procedure is the prevention of the reduction of ferric iron, which may occur because of the presence of metallic aluminium during the acid attack of the sample. The aluminium foil generally dissolves before the acid attack to the sample and immediately evolves hydrogen (this so called nascent hydrogen, has a reducing affect on ferric iron). It is, as is H_2 , useful for the removing the traces of air from the sample. Some of the undissolved aluminium may also be shared in the sample disintegration procedure and cause the reduction of ferric iron. Therefore, sometimes the value of ferrous iron may be a little high. Commonly, in routine analysis it is negligible. Alternatively the sample may be transferred without aluminium foil into the disintegration vessel. But the excess of HF, added later for the dissolution of the sample and the formation of an aluminium fluoride and ferric iron-fluorid complex, must be removed either by heating (F volatize as SiF_4 or H_2SiF_6) the solution, or adding a few ml of an aluminium solution into the disintegration vessel before the titration of ferrous iron.

The organic CO_2 may be recovered either from the total CO_2 (estimated by combustion) or from the inorganic- CO_2 (determined by means of an acid attack) by recalculation. Of course, it may be analyzed after recovery of the inorganic CO_2 in a further step by an acid treatment.

In the same manner, the concentration of ferric iron may be calculated after the recovery of the ferrous and total iron by means of volumetrical methods from the same solution (AYRANCI, 1979; MAXWELL, 1968). The weight of the sample aliquot used in the analysis depends on the concentration of components to be determined and naturally the sensitivity of the method used for the analytical procedures.

1.0–1.5 g of sample may be used for the estimation of lower concentrations (CO_2 and H_2O <1%) using a gravimetical method. A 0.5 g sample aliquot (ap-

prox.) is used for the recovery of higher concentrations (CO₂, H₂O >1%). The weight of the aliquot may be reduced to about 50–100 mg, if a homogeneous sample and a sensitive instrument (e.g. IR or gaschromatographical methods) is used. In the following table, some of the analytical results from the known standards, using the above presented method (gravimetrically) are given (Tab. 1). It must be noted that the analytical procedure, which is written here, deals with the combination of analytical methods used to recover components commonly needing individual analytical procedures. It doesn't propose to improve the sensitivity of any analytical method. The apparatus used in the procedure can be useful, not only for analysts working by wet-chemical methods, but also for the analysts using automated instruments (e.g. XRF, NAA, ICP, AAS). The financial costs of the apparatus is not much, if a tubular oven is present. The analysis of the above cited components of a rock sample may be carried out by using a gravimetric procedure and a normal tubular oven approximately in one hour, therefore allowing 6–7 samples to be analyzed in a day. The number of the analysis may be increased to 20 samples if a high frequency furnace and some automated instruments are present.

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Literature

- ABBEY, S. (1977): Studies in "standardsamples" for use in the general analysis of silicate rocks and minerals Part 5: 1977 edition of "usable values". Geol. Survey of Canada, paper 77-34.
- ALIMARIN, L.P. and B.I. FRID (1965): Quantitative mikrochemische Analyse der Mineralien und Erze. Steinkopff Leipzig.
- ANDO, A. et al. (1971): Compilation of data on rock standards JG-1, and JB-1 issued from the Geol. Survey of Japan, *Geochim. J.*, 5, 151.
- AUCOTT, J.W. and M. MARSHALL (1969): Quantitative determination of water in granites by infra-red analysis *Min. mag.* 37, 286, 256.
- AYRANCI, B. (1976): FeO-, Fe₂O₃- und SiO₂-Bestimmung im gleichen Aufschluss bei der Silikatanalyse. *Schweiz. Mineral. Petrog. Mitt.*, 56, 513.
- (1973): Die gleichzeitige Bestimmung von CO₂ und H₂O im Hauptkomponentenaufschluss von Silikaten, Abstract, *Fortschr. Miner.* 54; I-II, 5.
- (1979): Rapid direct and simultaneous determination of CO₂ and FeO in carbonate and silicate analysis, *Schweiz. Mineral. Petrog. Mitt.*, 59, 1/2, 95.
- BABA, Y. (1976): Microdetermination of carbon and hydrogen in organic compounds using flushed-oxygen combustion tube. *Microchem. Journal*, 21, 75.
- BAYER, E. (1962): *Gas Chromatographie*, Springer Verlag, Berlin.
- BELCHER, R. (1976): The elements of organic analysis. *Analyst* 101, 153.
- BERKA, A. et al. (1964): *Massanalytische Oxidations- und Reduktionsmethoden*, Akad. Verlagsgesellschaft, Leipzig.
- BOCK, R. (1972): *Aufschlussmethoden der anorganischen und organischen Chemie*. Verlag Chemie, Weinheim.

- (1974): Methoden der analytischen Chemie, Verlag Chemie, Weinheim.
- (1979): A Handbook of Decomposition Methods in Analytical Chemistr. 1. ed. International Textbook Company, London.
- BODROGAI, G. (1979): Über die CH-Bestimmungen in schwefelhaltigen Verbindungen, Mikrochim. Acta, 1, 47.
- BOUVIER, J. L. et al. (1972): Use of an "automatic sulphur titrator" in rock and mineral analysis: Determination of sulphur, total carbon, carbonate and ferrous iron. Geol. Surv. Canada paper 72, 31.
- BUSH, P. R. (1970): A rapid method for the determination of carbonate carbon and organic carbon. Chem. Geology 6, 59.
- CLEMENCY, C. V. and A. F. HAGNER (1961): Titrimetric determination of ferrous and ferric iron in silicate rocks and minerals. Anal. Chem. 33, 888.
- DIXON, B. E. (1934): The determination of carbon in rocks and minerals. Analyst 59, 739.
- DIXON, J. P. (1968): Modern Methods in Organic Microanalysis. Van Nostrano, London.
- DOLEZAL, J. ET AL. (1966): Decomposition Techniques in Inorganic Analysis. Elsevier, New York.
- DREIBUS, G. and B. SPETTEL (1976): Pyrohydrolyse zur Halogen- und Lithiumbestimmung in Gesteinsproben. Forsch. Mineral. 54 B. 1. 134.
- EASTON, A. J. (1972): Chemical Analysis of silicate rocks, Elsevier, New York.
- EHRENBERGER, F. und A. GORBACH (1973): Methoden der organischen Elementar- und Spurenanalyse, Verlag Chemie, Weinheim.
- ELLINGBOE, J. L. and J. E. WILSON (1964): Direct method for the determination of organic carbon in sediments. Anal. Chem. 36, 434.
- FARZANEH, A und G. TROLL (1977): Quantitative Hydroxyl- und H₂O-Bestimmungsmethode für Minerale, Gesteine und andere Festkörper, Z. Anal. Chim. 287, 43.
- FLANAGAN F. J. (1973): Values for international geochemical reference samples. Geochim. et Cosmochim. Acta, 37, 1189.
- FUNKE, A. und P. KLEINERT (1969): Über analytische Untersuchung an magnetischen Materialien. Z. Anal. Chem., 246, 362.
- GEL'MAN, N. E. et al. (1968): Quantitative analysis of heteroorganic compounds, simultaneous determination of carbon, hydrogen and heteroelement forming a volatile oxide, Zh. Anal. Khim. 23, 7, 1067.
- GILLBERG, M. (1964): Halogens and hydroxyl contents of micas and amphiboles in swedish granitic rocks. Geochim. et Cosmochim. Acta, 28, 495.
- GRANT, J. A. et al. (1963): The determination of carbon dioxide by non-aqueous titrimetry. Analyst, 88, 124.
- GROVES, A. W. (1951): Silicate Analysis, George Allen and Unwin, London.
- HERRMANN, A. G. and D. KNAKE (1973): Coulometrisches Verfahren zur Bestimmung von Gesamt-, Carbonat- und Nicht-Carbonat-Kohlenstoff in magnetischen, metamorphen und sedimentären Gesteinen. Z. Anal. Chem., 266, 196.
- HERRMANN, A. G. (1975): Praktikum der Gesteinsanalyse, Springer Verlag, Berlin.
- HEY, M. H. (1941): The determination of ferrous iron in resistant silicates. Min. Mag. 26, 116.
- Hillebrand, W. F. et al. (1953): Applied Inorganic Analysis. John Wiley, New York.
- HUGES, T. C. and P. HANNAKER (1978): The determination of carbon and hydrogen in geological materials by thermal decomposition. Chem. Geol. 22, 331.
- JEFFERY, P. G. (1975): Chemical Methods of Rock Analysis, Pergamon Press, Oxford.
- JEFFERY, P. G. and A. D. WILSON (1960): Closed circulation system for determining water, carbon dioxide and total carbon in silicate rocks in silicate rocks and minerals. Analyst, 85, 749.
- JEFFERY, P. G. and P. J. KIPPING (1964): Gas Analysis by Gaschromatography. Macmillan, New York.

- JOHNSON, W. M. and L. E. SHEPPARD (1978): A gravimetric method for the determination of H₂O+ in silicate rocks. *Chem. Geol.* 22, 341.
- JURCZYK, J. und G. LANZ (1969): Methoden der Eisen- und Manganeranalyse VEB, Leipzig.
- KISS, E. (1977): Rapid potentiometric determination of the iron oxidation state in silicates. *Anal. Chim. Acta*, 89, 33.
- KNOTT, A. C. and C. B. BELCHER (1975): Determination of carbon dioxide in coal and minerals. *Talanta*, 22, 751.
- KOLTHOFF, I. M. et al. (1978): *Treatise on Analytical Chemistry*, part II, vol. 10, John Wiley, New York.
- KOZŁOWSKI, E. and J. NAMIESNIK (1979): Determination of total carbon and total organic carbon from volatile air pollutants, V- determination of TC and TOC in laboratory air, *Mikrochim. Acta*, 1, 345.
- LATIMER, W. (1952): *The Oxidation States of the Elements and their potentials in Aqueous Solutions*. Prentice-Hall New York.
- LINDNER, B. und V. RUDERT (1969): Eine verbesserte Methode zur Bestimmung des gebundenen Wassers in Gesteinen, Mineralien und anderen Festkörpern. *Z. Anal. Chem.* 248, 21.
- MAXWELL, J. A. (1968): *Rock and Mineral Analysis*, Interscience, New York.
- MAZUREK-KOBYLINSKA, B. and E. KOZŁOWSKI (1978): Schnellbestimmung von C, H und S mit Hilfe der Entflammungsmineralisation. *Mikrochim. Acta*, 1, 137.
- MEYROWITZ, R. (1970): A microprocedure for the determination of carbon dioxide in minerals. USGS. Prof. paper 700C, 183.
- MONTGOMERY, H. A. C. and N. S. THOM (1962): The determination of low concentration of organic carbon in water. *Analyst*, 87, 1038.
- NOCHOLLS, G. D. (1960): Techniques in sedimentary geochemistry: Determination of ferrous iron contents of carbonaceous shales, *Journal Sed. Petrol.*, 30, 603.
- PECK, L. C. (1964): *Systematic Analysis of Silicates*. Geol. Surv. Bull. 1170, Washington
- RILEY J. P. and H. P. WILLIAMS (1959): The microanalysis of silicate and carbonate minerals: I. Determination of ferrous iron. II. Determination of water and carbon dioxide. *Mikrochim. Acta*, 4, 516 and 525.
- SCHAFFER, H. N. (1966): The determination of iron (II) oxide in silicate and refractory materials. *Analyst* 91, Part I, and II. 1089, and 763.
- SEIL, G. E. (1943): Determination of ferrous iron in difficult soluble materials. *Ind. Eng. Chem. Anal. Ed.*, 15, 189.
- SEN GUPTA, J. G. (1970): Determination of carbon by non-aqueous titration after combustion in high-frequency induction furnace. *Anal. Chim. Acta*, 51, 437.
- SHARPE, A. G. (1973): *Principles of Oxidation and Reduction*, Chem. Soc. London.
- SHOSTAKOVSKII, M. F. et al. (1968): Simultaneous determination of carbon hydrogen, and silicon in organosilicon compounds containing fluorine. *Zh. Anal. Khim.* 23, 5, 754.
- SIXTA, V. (1977): Coulometric determination of Carbonates in rock samples. *Z. Anal. Chem.* 285, 369.
- SMITH, F. G. (1942): *Cerate Oxidimetry*, G. F. Smith Chem. Co, Columbus, Ohio.
- STEGER, H. F. (1977): Oxidation of sulphide minerals I, determination of ferrous and ferric iron in samples of pyrrhotite pyrite and chalcopyrite. *Talanta*, 24, 251.
- VOLBORTH, A. (1969): *Elemental Analysis in Geochemistry*, A Major elements. Elsevier, New York.
- WILSON, A. D. (1960): The microdetermination of ferrous iron in silicate minerals by a volumetric and a colorimetric method. *Analyst*, 85, 823.
- WOLFF, G. (1964): Die Bestimmung von Karbonat in Mineralien und Gesteinen. *Z. Angew. Geol.* 10, 320.