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Autor: Ayranci, B.

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Simultaneous Determination of Inorganic-, Total-CO_2 and H_2O in routine Rock Analysis

by *B. Ayranci**

Abstract

A routine rapid analytical method is presented for the simultaneous determination of the inorganic-, total-CO_2 and H_2O 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 SO_3, SO_4, H_2O, CO_2 can not be carried out either by XRF or NAA or AAS. However, the total iron (as Fe_2O_3) 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, SO_4, CO_2, H_2O, As_2O_3) requires individual methods (e.g. colorimetrical volumetrical, gravimetrical 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-CO_2, and H_2O of the rock samples. The analytical methods commonly used to determine inorganic and total CO_2 and H_2O in the rock samples require two independent procedures:

* Institut für Kristallographie und Petrographie, ETH-Zentrum, CH-8092 Zürich.

1. The analysis of (inorganic-, organic-, total-) CO_2 is carried out after an acid treatment of the sample.
2. The recovery of total CO_2 and H_2O is performed by means of pyrolisis of the sample in a combustion technique.

For the determination of inorganic CO_2, the sample is dissolved by means of non-oxidizing acids. The organic and total CO_2 analysis are carried out by means of an oxidizing acid attack. The total CO_2 can also be calculated after the recovery of inorganic-, and organic CO_2 in succession; at first the inorganic CO_2 is recovered (after dissolving the sample by none oxidizing acids) and then the organic CO_2 is determined after adding a suitable agent (e.g. CrO_3) 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 CO_2 concentration also enables the simultaneous analysis of H_2O (GEL'MAN et al., 1968, RILEY et al., 1959); but the analysis of the inorganic and organic CO_2 of the sample by means of combustion train are complicated. The advantages of the pyrolisis 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-CO_2 and H_2O,furthermore the ferrous and total iron components of a sample may be analysed simultaneously, if an acid attack procedure (used for the recovering of CO_2 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 pyrolisis 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-CO_2 and the ferrous and total iron are recovered from the acid treatment, the total CO_2 and H_2O 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 CO_2 and

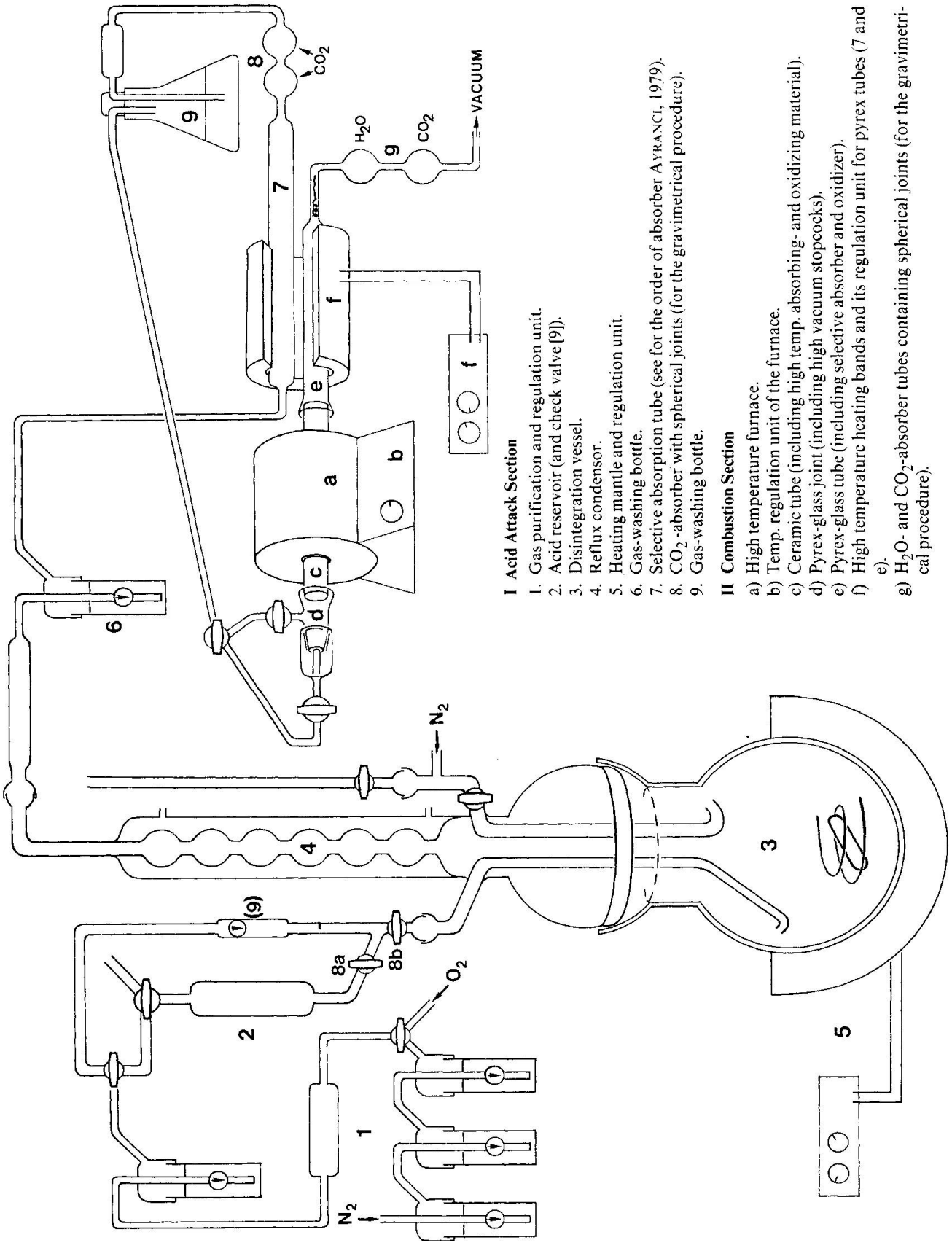

Fig. 1: A coupled acid attack and combustion train apparatus used for the simultaneous disintegration of sample aliquots by acids and pyrolisis procedures.

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 H_2O volatizing 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 H_2SO_4 (saturated by Ag_2SO_4). 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 adversly affect the analysis of CO_2 (e.g. H_2O, SO_2, H_2S, Cl, F, SiF_4, H_2SiF_6).
8. The absorption and recovery unit for CO_2 (e.g. volumetrical, gravimetrical supply).
9. A gas washing bottle, which contains concentrated H_2SO_4 and a guard tube (filled with ascarite). It is used to collect the carier 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 Al_2O_3 99.8%). This is about 650 mm long, its diameter is ca. 28 mm and open at both ends.
d. The pyrex-glass joint. Itr 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 CO_2 and H_2O (e.g. Cl, F, H_2S, SO_2, H_2SiF_6). 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 CO_2 and H_2O. The heating band may be regulated (by Herastat) up to 900 °C at given temperatures automatically.
g. The absorption and recovery units for CO_2 and H_2O (e.g. gravimetrical, volumetrical supply).

B – The Selection and The Packing of Absorbers

Several components (e.g. F, Cl, SO_2, SiF_4, Hg, H_2S, H_2SiF_6) which affect the analysis of CO_2 and H_2O 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 H_2O 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, CeO_2/La_2O_3 as efficient absorber for F, H_2SiF_6, As, P and CuO, Co_3O_4 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
2) Cu-gauze
3) CuO-wireform
4) Cu-gauze
5) CuO-wireform
6) $PbCrO_4$
7) $Ag_2(VO_3)$
8) $CuSO_4$ (Anhydrous on pumice)
9) Ag-wool
10) Ag_2O
11) $AgMnO_4$
12) Ag-wireform
13) Ag-wool
14) $AgMnO_4$
15) Ag-wool
16) NaF
17) MnO_2
18) $Mg(ClO_4)$ anhydrous
19) MnO_2
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, CeO_2/La_2O_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 H_2O. 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 H_2O 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. N_2 is intruduced, 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 H_2SO_4 + H_3PO_4). Air from the acid recervoir (2) is removed after turing 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 CO_2 and H_2O.

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 gravimetrical 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, contraining 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 condensor 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 °C and then gradually reduced over 20 minutes to 180 °C and then to 40 °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 °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 °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 gravimetrical 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 Weight of aliquots used in analysis (gr)	Recovered total H_2O%	CO_2%	Acid Attack Section Weight of aliquots used in analysis (gr)	Recovered Inorganic CO_2%	Recommended total H_2O%	CO_2%	References
USGS-SCo-1 Shale	0.200 0.250 0.500	6.2 6.2 6.35	3.4 3.25 3.55	0.200 0.200 0.300	2.6 2.5 2.65	6.3 (3.85+2.45*)	2.55+(0.18**)	FLANAGAN (1976) USGS Prof. Paper 840
USGS-MAG-1 Marine Mud	0.100 0.200 0.200	8.15 7.9 8.05	6.1 6.1 6.4	0.300 0.400 1.0	0.65 0.6 0.65	7.8 (5.22+2.58*)	0.51+(1.43**)	"
GSJ-JB-1 Basalt	0.250 0.300 0.400	2.05 1.90 2.05	0.24 0.25 0.24	0.200 0.400	0.25 0.2	1.98 (1.0+0.98*)	0.19	ABBEY (1972) FLANAGAN(1973) (s.literature)
CRPG-BR Basalt	0.300 0.400	2.85 2.7	1.0 0.95	0.300 0.400	0.8 0.85	2.80 (2.30+0.5*) 2.60 (2.30+0.30*)	0.9	ABBEY (1972) M. ROUBAULT et al. (1970) Sci.de la Terra Nancy
ZGI-BM**** Basalt	0.200 0.300	3.75 3.70	1.45 1.30	0.100 0.350	1.4 1.45	3.62***	1.34	FLANAGAN (1973)
ZGI-KH**** Limestone	0.100 0.150	1.1 1.05	37.9 37.8	0.05 0.100 0.100	37.4 37.55 37.8	1.0***	37.6	" (s.literature)
SSC-MRG-1**** Gabbro	0.400 0.500	1.08 1.05	1.15 1.10	0.500 0.600 0.300	1.0 1.05 1.08	1.02***	1.04	ABBEY et al. (1975) Canmet, Montreal

Abbreviations:
* H_2O^-
** organic C
*** H_2O^+
**** 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 gravimetrical method. A 0.5 g sample aliquot (ap-

prox.) is used for the recovery of higher concentrations (CO_2, H_2O >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 gravimetrical 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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