

**SIMULTANEOUS TG, DTG, DTA AND EGA TECHNIQUE FOR
THE DETERMINATION OF CARBONATE, SULPHATE, PYRITE
AND ORGANIC MATERIAL IN MINERALS, SOIL AND ROCKS
III. Operation of the thermo-gas-titrimetric equipment and the
examination procedure in special cases**

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When the organic matter or sulphide content of a mineral is above a given limit (e.g. in chalcogenides or shaly coal), its burning under conventional conditions is not complete, sulphur and pyrolysis products being deposited on the colder parts of the equipment.

In order to eliminate this error source, changes have been made in the construction of the equipment for simultaneous TG, DTG, DTA and EGA (derivatograph). This part of the series describes the construction of the modified version of the apparatus, its operating principle and the changes in the experimental conditions.

With the technique and equipment described in Part II of this publication [1], it was found that the carbonate and sulphate contents of mineral substances could be determined with sufficient accuracy even if the sample contained small amounts of pyrite or organic matter. However, if the amounts of these latter components exceeded a certain limit or they were even present as major components, the incomplete burning led to sulphur and pyrolysis product formation and deposition on the colder parts of the equipment. This naturally distorts the results.

Such an error occurs in only a small percentage of the many possibilities of application.

However, the method bears on such important fields as the analysis of chalcogenides, or carbon determination in shales rich in organic matter. We therefore made the measuring technique suitable for the performance of such tasks too. The present paper reports on the necessary changes in the construction of the apparatus and in the examination procedure in these special cases.

1. Conditions for establishing an oxygen-free gas atmosphere

The gas-gap formed at the edge of the lower corundum diaphragm disc (10) and of the boring (12) of the furnace stand of the apparatus (Fig. 1) allows attainment of an oxygen-free gas atmosphere (e.g. N₂, Ar) of high purity. This is necessary in the

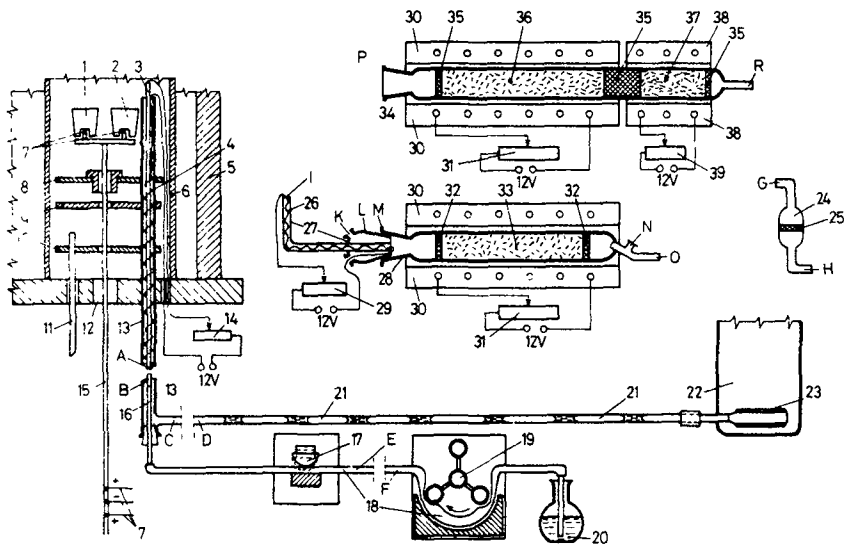


Fig. 1 Derivatograph modified for testing minerals with pyrite and/or organic material content.

1. crucible for the sample; 2. crucible for the reference material; 3. corundum capillary tube for holding the platinum heating spiral; 4. platinum heating spiral; 5. electric furnace; 6. corundum bell; 7. thermo-couples; 8. upper corundum diaphragm disc; 9. middle corundum disc; 10. lower corundum diaphragm disc; 11. corundum gas inlet tube; 12. boring of the furnace stand; 13. corundum gas outlet tube; 14. variable resistor; 15. capillary tube for conducting the wash-water; 17. periodical injector; 18. rubber tube; 19. peristaltic pump; 20. wash-water; 21. capillary tube for gas conducting; 22. absorption vessel; 23. glass filters; 24. sulphur trap; 25. glass filter; 26. platinum heating spiral; 27. silica joining nipple with ground stopper; 28. silica tube for second-burning; 29. variable resistor; 30. electric furnace; 31. variable resistor; 32. asbestos stopper; 33. silica gel or cobalt(III, II) oxide or Hopcalite catalyst packing; 34. heat-resistant glass tube for second burning; 35. asbestos stopper; 36. copper(II) oxide wire coated with lead chromate; 37. lead dioxide packing; 38. electric furnace; 39. variable resistor

determination of the metal sulphide and organic matter contents of the sample. Here, besides the careful regulation of the inlet and outlet rates of the carrier gas flow, it must be considered that even commercial "high purity" nitrogen and argon may contain oxygen in trace amounts.

The purification of inert gases from their oxygen content is easiest with the help of the oxygen-binding product circulated by BASF (Badische Anilin und Soda Fabrik) under the name "BTS catalyst". This preparation, which contains metal oxides (MnO , CrO , etc.), readily binds oxygen even at room temperature. It is therefore sufficient to put the granules into a glass flask and to insert this between the fine gas-valve and the gas-purifier glass flask filled with soda-asbestos (see Fig. 1 in Part II). Then the carrier

gas is simply conducted at room temperature through this arrangement. The BTS catalyst can be regenerated in a hydrogen gas flow.

To make the gases oxygen-free, a "copper furnace" can also be used (point (a) in the Addendum). If the possibility arises that in spite of the precautions air is entering the reaction space, the error can be found by applying the experiment described in point (b) of the Addendum.

2. In the event of sulphur vapour formation a sulphur gap should be used

If not only the total sulphur content, but also the sulphate impurities of pyrite must be separately identified and determined, the sample must be heated in an oxygen-free atmosphere. In an inert gas atmosphere the pyrite undergoes disproportionation and sulphur vapour is liberated. On coming into contact with water, the sulphur separates out in solid form, and may with time clog the gas outlet tube (13), the capillary tube (21) and the glass filter (23) of the absorption vessel of the apparatus (Fig. 1). It is therefore advisable to insert a sulphur trap (24) (connections between points *A-B*, *C-G*, *H-D* and *E-F*) between the gas outlet tube (13) and the capillary tube (21). This is actually a glass vessel divided into two parts by means of a rough glass filter (25) of minute resistance. This filter retains the sulphur, which can easily be removed with solvents, e.g. carbon disulphide, after every experiment.

The procedure is also suitable to the partial floating out of the tar formed of the organic compounds in the course of the procedure and deposited on the colder parts of the tubes.

3. Error due to the formation and incomplete burning of sulphur vapour, and elimination of this

If pyrite is examined at the conventional heating rate of 10 degree min^{-1} , it may occur that the formed sulphur vapour does not completely burn, even when oxygen is applied as carrier gas. In the course of the burning great amounts of heat are liberated, and the temperature of the sample rises spontaneously and uncontrollably far above the neighbouring temperature. Due to this, the decomposition accelerates to such an extent that a local oxygen absence arises and the sulphur vapour can only partly burn. The unburned sulphur vapour is transported by the carrier gas and condensed on the colder parts of the apparatus.

The error can be eliminated if the unburned sulphur vapour is subsequently burned in an appropriate manner. In this case a silica second-burning tube (28) and its silica joining nipple with ground stopper (27) are inserted (connections: between points *A-I*, *L-M* and *O-D*) after the heated gas outlet tube (13). The silica joining nipple (27) is also heated by means of a platinum spiral (26) in order to prevent the condensation of sulphur vapour in the tube. The second-burning tube (28), which

heated up to 500–700° by means of an electric furnace (30), is packed with silica gel (33). This ensures that the molecules of sulphur vapour undergo continual collision and reside for a long time in the high-temperature space, where at last they combine with oxygen. Instead of silica gel, the second-burning tube (28) can also be packed with silica wool.

If it may be assumed that sulphuric acid or sulphur trioxide are formed in the course of the test, flushing must be applied to prevent their possible condensation. In this case the peristaltic pump (19) which serves for the addition of water is connected with the second-burning tube (28) (connection: between points *N–F*).

In the case of samples with high sulphur contents further oxygen amounts (5–10 l h⁻¹) can be introduced into the system at joining point *K* of the ground stopper of the second-burning tube (27). Of course, the rate of gas exhaust must then be increased correspondingly.

4. Determination of organic components in the absence of sulphur compounds

The determination of organic impurities in mineral substances is based on the fact that organic materials burn quantitatively to carbon dioxide and water in an oxygen atmosphere. From the amount of carbon dioxide produced, the amount of the organic component can be estimated. However, the burning of organic materials is seldom complete and various quantities of carbon monoxide and saturated and unsaturated hydrocarbons are also formed, together with pyrolysis products that are volatile at the test temperature and liquid at room temperature. The latter condense on the colder part of the gas outlet tube. This phenomenon reduces the amount of carbon dioxide.

It is found that if the sample contains only small amounts (0.5–2.0%) of organic matter, the error in respect of organic substance is in the range 1–5%. Consequently, the relative error in respect of the sample weight can be neglected. However, the error may be eliminated completely if, analogously as in elementary C–H analysis in organic chemistry, the burning is rendered quantitative by the use of a catalyst.

In such instance the mixture of oxygen carrier gas and the gaseous decomposition product is conducted through a second-burning tube (28) made from heat-resistant glass or silica, which is filled with granulated cobalt(III, II) oxide catalyst (product of Carlo Erba) (connections: between points *A–I*, *L–M* and *O–D*). The temperature of the tube is kept at 400–600° by means of the electric furnace (30). Since the burning is complete only in an oxygen-rich atmosphere, further oxygen amounts are conducted into the second-burning tube through joint *K* at a rate of 5–10 l h⁻¹. In this case the rate of gas exhaust must be increased to the same extent. The catalyst in the tube causes the volatile organic compounds to burn completely and carbon dioxide is formed quantitatively from them. Any carbon monoxide formed is also oxidized to carbon dioxide on the catalyst surface.

The described technique is suitable only if it is certain that there are no sulphur-containing components in the sample, i.e. the formation of sulphur dioxide or sulphur

trioxide can be discounted, for cobalt(III, II) oxide binds these gaseous products only partly, so that the values obtained for both the sulphur and the carbon content would be erroneous.

Hopcalite or silver permanganate catalyst can be applied as packing instead of cobalt(III, II) oxide if its temperature is kept at about 200°.

5. Determination of organic substances in the presence of sulphur-containing minerals

If the sample contains sulphide or sulphate mineral components besides the organic matter, the determination is carried out in two experiments in the following way in order to eliminate the error.

First, the sulphur trioxide is determined in an oxygen atmosphere by the already described procedure, but with omission of the second-burning with cobalt(III, II) oxide catalyst. Rinsing with water is applied (connections: between points *A-B*, *C-D* and *E-F*). The titration must be carried out at pH 4. In this way the burning of the organic matter will not be complete, but this is not necessary at all, for at pH 4 the carbon dioxide departs unmeasured from the system.

In a second experiment the carbon dioxide formed is determined, care being taken that the organic matter is burned completely in a catalytic second-burning and that simultaneously the sulphur trioxide and sulphur dioxide formed are bound (connections: between points *A-I*, *L-P* and *R-D*). The titration is carried out at pH 9.3, when only the carbon dioxide consumes titrant.

The catalytic burning of organic compounds and the simultaneous and quantitative binding of sulphur compounds may be carried out according to the Pregl method applied for C-H determination in organic chemistry.

In this case the second-burning tube (34) made from heat-resistant glass contains two kinds of packing. That promoting oxidation consists of copper oxide + lead chromate (36) (Addendum, point (c)), while the lead dioxide packing (37) serves for the binding of sulphur tri- and dioxide. The former packing is heated up to 600° by an electric furnace (30), and the latter one by another furnace (38) up to 200°. The temperatures of the furnaces should be kept at a constant value.

6. Conversion of carbon monoxide to carbon dioxide

A characteristic property of carbonate minerals, which decompose above 1000°, is that carbon monoxide is formed in the course of their decomposition in oxygen-poor or oxygen-free atmospheres [2]. In such cases application of the second-burning tube (28) is necessary; in this instance it is filled with Hopcalite catalyst, consisting of a mixture of copper, manganese, cobalt, nickel and silver oxides and peroxides (connections: between points *A-I*, *L-M* and *O-D*). (The Hopcalite catalyst is one of

the agents of gas-masks.) It is advisable to heat the Hopcalite packing, because the process can take place quantitatively and rapidly only at 100°.

Addendum

(a) Preparation of "copper furnace"

A silica tube 20 mm in diameter is filled with the "wire-shaped" copper oxide used for C-H determinations in organic compounds. The packing, about 200–400 mm in length, is heated by an electric furnace up to 500° while the copper oxide is reduced to metallic copper in a hydrogen flow. The resulting metallic copper has a high active surface area, which at 500° binds even traces of oxygen.

(b) Detection of trace amounts of oxygen in inert carrier gases

It is possible to prove in a given case that the atmospheric oxygen cannot enter the corundum bell (6) of the apparatus, and also that the BTS catalyst makes the inert carrier gas oxygen-free. The control examination is based on the observation that manganese(II) oxide rapidly binds even traces of oxygen at about 500°. Figure 2 illustrates the results of such an experiment. Manganese(II) oxide was prepared from

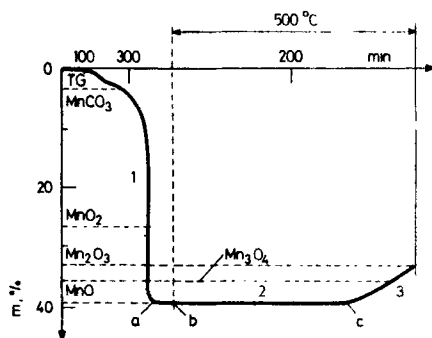


Fig. 2 TG curve of manganese(II) oxide, proving the absence of oxygen from the inert carrier gas

basic manganese(II) carbonate by thermal decomposition within the crucible of the derivatograph. The sample was heated to 500° in a carefully purified oxygen-free nitrogen atmosphere, the temperature increase (point *b*) was stopped, and the sample was kept at 500° for 5 hours. During this period the weight of the sample did not change, proving that oxygen in the air could not pass through the air gap into the corundum bell and that the inert carrier gas did not contain oxygen impurities (section *b–c*). Subsequently the introduction of carrier gas was interrupted (point *c*), whereupon the weight of the sample slowly began to increase, proving that air slowly

passed into the corundum bell, the manganese(II) oxide being oxidized to manganese(III) oxide.

(c) Preparation of copper oxide-lead chromate

The copper oxide -- lead chromate preparation used in organic microanalysis is commercially available. In the laboratory it can be prepared in the following way: One weight fraction of "wire-shaped" copper oxide is heated up to 800° in an iron vessel, and one weight fraction of lead chromate powder is scattered upon it during mixing. In this procedure the lead chromate forms a well adhering and uniform coating on the copper oxide.

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References

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Zusammenfassung — Wenn der Gehalt eines sulphidischen Minerals an organischen Material eine gegebene Grenze überschreitet (z.B. in Chalcogeniden oder in Kohlenschiefer), so ist die unter herkömmlichen Bedingungen ausgeführte Verbrennung nicht vollständig und Schwefel sowie Pyrolyseprodukte scheiden sich in den kälteren Teilen der Apparatur ab. Um diese Fehlerquelle auszuschalten wurde die Konstruktion der Apparatur für simultane TG, DTG, DTA und EGA (Derivatograph) abgeändert. Die modifizierte Version des Gerätes sowie dessen Arbeitsprinzipien und die Veränderungen in den experimentellen Bedingungen werden beschrieben.

Резюме — Сгорание органического вещества при его высоком содержании в таких сульфидсодержащих минералах, как например, халькогениды и сланцы, протекает неполностью, поскольку продукты пиролиза и сера осаждаются на более холодных частях прибора. С целью устранения этого источника ошибок были внесены изменения в конструкцию аппаратуры, предназначенной для совмещенных ТГ—ДТГ—ДТА—АВГ. В статье описывается изменение конструкции аппаратуры, принцип ее действия и изменения экспериментальных условий.