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

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This part of the series deals with a description of the thermo-gas-titrimetric (TGT) unit of the equipment for simultaneous TG, DTG, DTA and EGA (derivatograph). It also provides detailed information about the experimental conditions to be applied in order to obtain accurate and reproducible results.

The measuring technique is based on the thermo-gas-titrimetric (TGT) determination of carbon dioxide and sulphur trioxide, respectively. Although this technique has been known for a long time [1—3] and has been used to clarify the kinetics and mechanisms of the decompositions of many compounds [1], the extension of its application to the selective determination of carbonate, organic matter, sulphide and sulphate in minerals, in the presence of one another, involved a series of problems. In order to eliminate these difficulties, minor modifications in the construction and operation of the derivatograph became necessary. In our present paper we wish to describe the modified version of the apparatus and its operation technique.

Construction and operation of the device

A schematic representation of the derivatograph and of the attached TGT device can be seen in Fig. 1. With the equipment, the weight change of the sample (TG), the rate of weight change (DTG), the enthalpy change (DTA), the changes in the amount of gaseous products liberated from the sample (TGT) and the rate of this latter (DTGT) can be measured simultaneously. The register device records the five variables either against time or against temperature. The TG, DTG and DTA curves are taken in the way already known [1]. Here, therefore, we omit a description of this, and deal with the question of determining the gaseous decomposition products, which takes place according to the following principle.
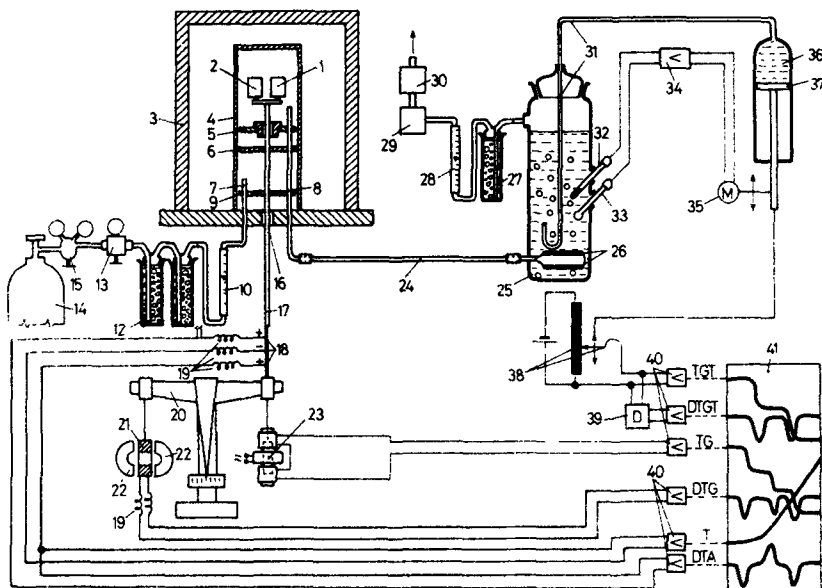
Fig. 1 Derivatograph for simultaneous TG, DTG, DTA and EGA. 1. crucible for the sample, 2. crucible for the reference material; 3. electric furnace; 4. corundum bell; 5. upper corundum diaphragm disc; 6. middle corundum diaphragm disc; 7. corundum gas inlet tube; 8. corundum gas outlet tube; 9. lower corundum diaphragm disc; 10. gas flow meter; 11. bottle filled with silica gel for gas drying; 12. bottle filled with soda asbestos (ascarite) for gas purification; 13. governor valve for the control of carrier gas flow; 14. gas cylinder; 15. reducer valve of the gas cylinder; 16. boring of the furnace stand; 17. corundum tube for holding the thermo-couples; 18. thermo-couples; 19. flexible conductor; 20. balance, 21. coil of the deriving unit; 22. magnets of the deriving unit; 23. differential transformer; 24. capillary tube for gas conducting; 25. absorption vessel; 26. glass filters; 27. bottle fillled with silica gel for gas drying; 28. gas flow meter; 29. control unit for gas flow; 30. vacuum pump; 31. inlet tube for the titrant; 32. reference calomel electrode; 33. glass electrode; 34. pH-meter switch; 35. servomotor of the automatic burette; 36. cylinder of the automatic burette; 37. piston of the automatic burette; 38. potentiometer; 39. deriving device; 40. pens of the recorder; 41. chart of the recorder

The temperatures of the sample (1) and of the reference material (2) (as a rule aluminium oxide ignited at least at 1500°), both situated in platinum crucibles, are increased by an electric furnace (3) at a uniform rate. The temperature can be increased up to 1500°. The liberated gases, in the present case carbon dioxide and sulphur trioxide, respectively, are conducted by a carrier gas to the absorber vessel (25) through a stiff but somewhat flexible polyethylene or glass capillary tube (24). In the absorber, the gaseous mixture is bubbled through water, which absorbs the gaseous decomposition products, carbonic acid and sulphuric acid being formed. The pH of the solution changes, which is sensed by a glass (33) and calomel reference (32) electrode pair, and by the pH-meter (34) joined to their poles. In this latter a regu-

lating device is incorporated, which sets into operation the automatic burette (35, 36, 37) as soon as the pH of the absorption solution reaches the value selected in advance. The burette (36, 37) adds titrant to the absorption solution for as long as a difference exists between the selected and measured pH values (pH-stat titration). The speed of the titration is proportional to the difference between the measured and selected pH values. Accordingly, if the gas evolution accelerates, the addition of the titrant also accelerates, and vice versa. The piston (37) of the automatic burette also operates the sliding of a potentiometer (38). The signal of the potentiometer, which is proportional to the volume of titrant consumed, and to the amount of the gaseous decomposition product liberated, is drawn by a recorder device (40, 41) as a function of time or temperature. In this way the TGT curve is obtained. On derivation of the signal of the potentiometer by means of a deriving device (39), the DTGT curve is obtained, which illustrates the changes in rate of the liberation of gaseous decomposition products.

Procedure

Since the developed technique is more complicated than the average, the procedure to be followed will be described in more detail than is usual. In order to get accurate and reproducible results [4, 5], it must be ensured that
— carbon dioxide and sulphur trioxide develop in an amount proportional to the relevant mineral component;
— these gaseous products should pass into the absorption vessel without delay or loss;
— the error caused by the poor absorption of the gaseous products in water should be eliminated by applying the correction and compensation methods resp.
It is clear that the prescribed experimental conditions must be kept strictly constant.

1. Since the system surrounding the sample is actually an open one,
it is especially important to take meticulous care in collecting the
gaseous decomposition products quantitatively

Experience shows that, for the given construction of the gas-collecting system, if carrier gas is introduced in excess through a corundum gas inlet tube (7) between the middle (6) and lower (9) corundum diaphragm discs, while the mixture of carrier gas and the gaseous product is exhausted at a rate of 10 l h^{-1} from the upper space of the corundum bell (4), through a corundum gas exhaust tube (8), then a gas-gap is formed at the edge of the upper (5) and middle (6) diaphragm discs. The discs significantly decrease the cross-section of the corundum bell. The flow of the carrier gas accelerates significantly through the free slit, which prevents the gaseous product from entering the lower space of the corundum bell (4) and leaving the system from there.

2. If the rates of the gas flow introduction and exhaustion are correctly selected,
   air can be prevented from entering the bell

The absence of air is a fundamental condition for the accurate determination of carbon dioxide, as air always contains carbon dioxide in amounts of about 0.03%. However, laboratory air may also contain other gaseous contaminants, such as HCl, NH_3 and SO_2, which would falsify the results of both carbon dioxide and sulphur trioxide determination.

If the carrier gas is introduced at a rate of 40 l h^{-1} and exhausted at a rate of 10 l h^{-1} for example, the excess of carrier gas flows downward the edge of the lower diaphragm disc (9), after it outward through the narrow boring (16) of the furnace stand at a rate of 30 l h^{-1}.

This relatively rapid gas flow prevents air from entering the bell. At this point of the gas collector system a gas-gap is similarly formed.

In order to ensure the efficacy of the gas-gap, both the introduction and extraction of the gas must be kept at a constant rate. The stability of the former is ensured by a fine control valve (13), and that of the latter by an automatic control unit (29). The stability of each is controlled by means of a gas flowmeter (10, 28).

3. Before use, the carrier gas must be purified from interfering gaseous
   contaminants

Even commercial gases (N_2, Ar, O_2) claimed to be of high purity may contain trace amounts of carbon dioxide. Especially in the case of carbon dioxide determinations therefore, it is very important that the carrier gas should be conducted through a gas-purified glass bottle (12) filled with soda-asbestos (ascarite). If work is to be performed in air atmosphere, it is also necessary that the air applied as carrier gas be purified from its alkaline contaminants (e.g. NH_3) by means of a phosphoric acid-containing gas purifier. Any acid-forming gaseous contaminants in the laboratory air (e.g. SO_2, SO_3 and HCl) will be bound by the soda-asbestos.

Gas purifiers (11, 27) filled with silica gel ensure the correct operation of the gas flowmeters (10, 28). Otherwise, water from the wet gas flow could condense within the meters, which would render measurement of the rate of carrier gas flow inaccurate.

4. The collected gaseous decomposition products must be conducted quantitatively
   and without delay into the absorber vessel

The cross-section of the gas outlet (8) and capillary tubes (24) is small, and their inner volume is insignificant, so in the case of carbon dioxide the difference between gas formation and its observation is only 20–30 s. This phase delay is short even if water vapour is liberated simultaneously. Although part of the water vapour may condense in the colder parts of the tube system, this does not cause any error since the amount of condensed water is small and the solubility of carbon dioxide in water is insignificant.

However, experience shows that the transport of sulphur trioxide involves trouble, for sulphur trioxide (partly as a liquid, or seldom as a solid) condenses at the cooler part of the gas outlet tube (8), or possibly in the capillary tube (24). If water vapour is liberated simultaneously sulphuric acid is formed, which also condense in the gas outlet tube. This can leave only if the increasing furnace temperature causes the colder part of the outlet tube (8) to attain the boiling point temperature of concentrated sulphuric acid, i.e. about 300°. It is found that this takes place only in the later stages of the examination, when the temperature of the furnace has reached 600—700°. Accordingly, the phase delay between the formation and observation of sulphur trioxide may relate to a temperature difference of even several hundred degrees. The condensed sulphur trioxide and sulphuric acid cannot depart from the capillary outlet tube (24) even in the later stages of the experiment.

The error can be eliminated with the structural modification of the device shown in Fig. 2, and with the application of the following preventive measures. A platinum filament (43) wound on a capillary corundum tube (42) must be placed in the gas outlet tube (8) from above. The platinum wire is heated by an electric current. By means of a variable resistance (44), the voltage is changed so that the colder part of the gas outlet tube, outside the furnace, is also heated to about 300° in order to prevent the condensation of sulphuric acid there. Further, through a capillary tube (45) the peristaltic pump (48) periodically pumps sufficient (5—10 ml h^{-1}) wash-water (49) into the gas outlet tube (8), so that the whole cross-section of the capillary tube (24) is washed by the drops collecting from time to time (2—3 drops min^{-1}) and running through one after another. Another dosing device, the periodical injector (46) hits the wash-water-conducting rubber tube (47) every 10 seconds, causing a drop (about 0.05 ml) of wash-water to spirt periodically onto the glowing platinum wire (43). This prevents sulphuric acid from remaining in the dead space between the platinum wire and the muzzle of the dosing tube (45). The polyethylene capillary tube (24) must be situated in such a way, that no water pocket should be formed in which wash solution could collect.

The described equipment and procedure do not interfere with the carbon dioxide determination, and their use is advisable even when it is only suspected that sulphur trioxide may also be formed besides carbon dioxide or sulphur dioxide.

5. The factors influencing the absorption of the gaseous decomposition products

Sulphur trioxide and especially carbon dioxide are absorbed poorly by water, the former because it forms a fog with water vapour, and the latter because it dissolves only slightly in water.

The glass filter (26) of the absorption vessel (25) greatly influences the absorption of gaseous decomposition products in water, for a gas mixture pumped through it becomes split into fine bubbles. The smaller the bubbles, the more complete the absorption. Different absorption vessel may therefore lead to different examination results (see Part IV and in fig. ....) ....
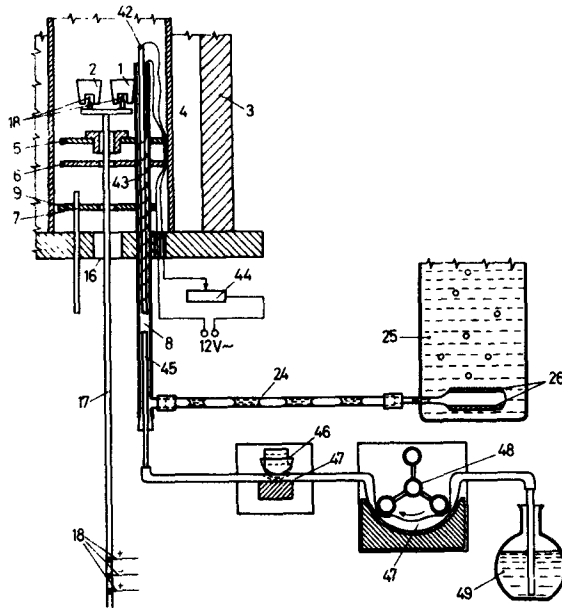(26) is lim ted by the surface ....

Fig. 2 Derivatograph modified for examination of sulphur containing minerals. 1. crucible for the
sample; 2. crucible for the reference material; 3. electric furnace; 4. corundum bell; 5. upper
corundum diaphragm disc; 6. middle corundum diaphragm disc; 7. corundum gas inlet tube;
8. corundum gas outlet tube; 9. lower corundum diaphragm disc; 16. boring of the furnace
stand; 17. corundum tube for holding the thermo-couples; 18. thermo-couples; 24. capillary
tube for gas conducting; 25. absorption vessel; 26. glass filters; 42. corundum capillary tube
for holding the heating spiral; 43. platinum heating spiral; 44. variable resistor; 45. inlet
capillary for wash-water; 46. periodical injector; 47. rubber tube; 48. peristaltic pump;
49. wash-water

presents to the gas flow. After the glass filter, therefore, a larger depression must be
created. However, this involves the danger that air may enter the system at the cocks,
joints and packing of the burette piston. The possible appearance of bubbles in the
burette can be attributed to this.

   If surface tension-decreasing materials, such as ethyl alcohol or methyl alcohol, are
added to the water, the magnitude of the bubbles formed on the glass filter decreases
sharply and the absorption increases proportionally (see Part V of the publication).
In order to render the absorption of the gases complete therefore, ethyl alcohol must
always be added to the absorption solution.

   The absorption of the gaseous decomposition products also depends on their con-
centration in the exhausted gaseous mixture. Consequently, in the interest not only
of the gas-gap to be formed on the edges of the diaphragm discs [5—7], but also of
the sufficient absorption of the gaseous products, it must be ensured that the rate of
the gas be kept strictly constant.

The hydrogen ion concentration of the absorption solution must not vary by more than ± 0.1 pH unit during the carbon dioxide determination (see Part V of the publication). This must be allowed for in the selection of the magnitude of the sample and the rate of heating. Experience shows that if the rate of absorption of carbon dioxide in the absorption solution is greater than $2-5$ mg min^{-1}, the pH of the solution drops below 9.2, and the efficiency of the absorption decreases, while the amount of carbon dioxide departing unmeasured from the system increases.

6. Composition of the absorption solution before the beginning of the carbon dioxide determination

> 400 ml distilled water,
> 7 ml ethyl alcohol,
> 10 ml 0.1% sodium hydrogen carbonate solution,
> 10 drops phenolphthalein indicator.

Before the experiment the titration device automatically adds sodium hydroxide titrant to the above neutral solution until its pH value becomes exactly 9.3.

Sodium hydrogen carbonate is added to the solution so that the titration should not begin in an ion-poor solution, since the operation of the glass electrode is uncertain in such solutions. However, too much sodium hydrogen carbonate exerts a buffer effect and causes an error (see Part V of the publication).

The indicator serves only for the visual control of the pH of the solution.

The composition of the wash solution must be identical with that of the absorption solution at the beginning of the examination.

7. Composition of the absorption solution before the beginning of the determination of sulphur trioxide and sulphur dioxide

> 400 ml distilled water,
> 5 ml hydrogen peroxide (30%),
> 7 ml ethyl alcohol,
> 10 ml 0.1% sodium sulphate solution,
> 10 drops methyl red + methylene blue indicator,
> 0.1 ml N hydrochloric acid.

Before the experiment the titration device automatically adds sodium hydroxide titrant to the above acid solution until its pH value becomes exactly 4.

In the vicinity of $700-800°$ sulphur trioxide decomposes significantly to oxygen and sulphur dioxide. In the examination of sulphur-containing compounds, therefore hydrogen peroxide must always be added to the absorption solution to oxidize sulphurous acid to sulphuric acid. Otherwise, with oxygen or air as carrier gas, the absorption solution would dissolve enough oxygen for the oxidation of sulphurous acid to sulphuric acid. In these cases the hydrogen peroxide is added only for safety's sake.

On the simultaneous measurement of carbon dioxide and sulphur trioxide, care must be taken that the applied hydrogen peroxide should not contain any metal

phosphates as stabilizers, since these would render the measurement uncertain. In this case the titration must be performed at pH 9.3, in which pH range the metal phosphates operate as buffers.

8. Control of the correct operation of the pH-meter

Whether or not the pH-meter shows the real values must be checked before every measurement with a buffer solution. If necessary, the normal position of the pH-meter must be corrected. It is advisable to check by using buffers the pH of which is near to 9.3 and 4 resp.

This control must be performed with special care in the case of carbon dioxide determination (see Part V of the publication).

## 9. Preparation and storage of 0.1 N NaOH titrant, and establishment of its titre

It is advisable to use as titrant carbonate-free 0.1 N NaOH solution prepared according to Kolthoff (see point (d) of the Addendum). Sodium carbonate impurity renders the titre determination far too complicated. This is demonstrated in Table 1 (point (e) of the Addendum), which lists the titre values of a sodium hydroxide solution containing a small amount of carbonate determined under various conditions.

It is easy to see that carbonate impurity in the titrant causes error only if the sodium hydroxide is titrated with hydrochloric acid and not vice versa, and if the given titre (t_I or t_{II}) is used for the calculation of the sulphate and carbonate contents at the appropriate pH value.

Table 1 Titers of sodium hydroxide titrant containing small amount of carbonate

Titrated	Methyl red– methylene blue mixture	Phenolphthaleine	
		without boiling	after repeated boiling
Base with acid	t_I = 1.0000	t_{II} = 0.9731	t_{III} = 0.9995
Acid with base	t_{IV} = 1.0014	t_V = 1.0002	–

In the case of sulphate determination, the titration is carried out as if no sodium carbonate impurity were present at all. Accordingly, if both the determination of the titre (t_I) and the TGT examination are carried out in the vicinity of pH 4, the sodium carbonate reacts with two equivalents of the acid:

$$Na_2CO_3 + 2 HCl = 2 NaCl + H_2O + CO_2 \tag{1}$$
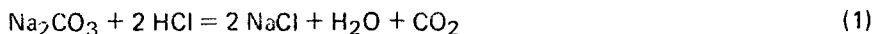
If carbon dioxide determination is performed, then sodium carbonate reacts only with one equivalent of the acid, since both the titre establishment (t_{II})

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \tag{2}$$

and the TGT examination

$$Na_2CO_3 + H_2CO_3 = 2\,NaHCO_3 \tag{3}$$

are carried out in the vicinity of pH 9.3. Under these conditions the reaction occurs only until the formation of sodium hydrogen carbonate.

On this basis, it is easy to see that it is most reasonable to work with carbonate-free alkali, for in this case the error source can be eliminated completely.

The glass vessel from which the automatic burette is filled up with titrant is closed with a vent pipe packed with soda-asbestos. In this way the air replacing the exhausted titrant will be free of carbon dioxide. Otherwise, the subsequently absorbed carbon dioxide would change the titre of the sodium hydroxide solution, which must be taken into account in the case of carbon dioxide (reactions 2 and 3), but can be neglected in the TGT examination of sulphur trioxide (reaction 1).

10. It is expedient to check the correct operation of the device from time to time by calibration measurements

The control examinations should be carried out with a calibration material which can be prepared with stoichiometric composition. As a consequence, in the course of the examination exactly known amounts of carbon dioxide and sulphur trioxide can be liberated. As calibration materials, potassium hydrogen carbonate can be used advantageously in carbon dioxide determination (Part V of the publication), as can copper sulphate pentahydrate in sulphur trioxide determination (Part IV of the publication). Both standard compounds can be purified by repeated recrystallization. Potassium hydrogen carbonate can be purified also according to point (c) in the Addendum.

The calibration measurements for the control must be performed under the very same experimental conditions as used for the determination of the correction factor and for the examination of the unknown material.

The effects of the experimental conditions upon the results will be discussed in detail in Parts IV and V of our publication.

Addendum

(a) Control of the purity of the carrier gas by means of a blank test

The fact that the carrier gas does not contain interfering foreign gases and that the carbon dioxide of the air has not entered its flow can easily be proved in a blank test. The TGT curve in Fig. 3 shows the result of such an experiment at pH 9.3. In the beginning (curve section $a-b$), carrier gas purified as described above was conducted through the device. According to the curve here (between points a and b) no titrant was consumed, demonstrating that the system worked regularly. Thereafter (section $b-c$), the rates of the gas inlet and outlet were changed so that about 10% of air from

the atmosphere should be mixed with the carrier gas. Later (section $c–d$) the intro-
duction of the carrier gas was stopped and the device pumped air through the absorber
vessel for an hour. These experiments prove that even very small amounts of per-
meating air may cause error. After the introduction of air, pure carrier gas was again
conducted (point d) through the apparatus. Thereafter no titrant was consumed.
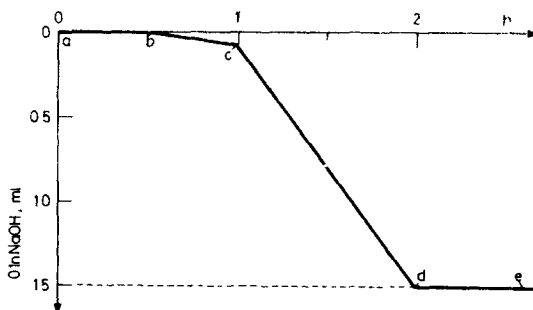

Fig. 3 The purity of the carrier gas showing TGT curve obtained in a blank test

(b) Handling of glass and calomel electrodes

Before its first application, the glass electrode must be soaked for at least 24 hours
in 0.1 N hydrochloric acid in order that the surface of the glass membrane becomes
swollen. Between two measurements it is also advisable to keep the glass electrode in
dilute hydrochloric acid solution.

Before every measurement it must be checked whether a sufficient amount of solid
potassium chloride remains inside the calomel electrode. If this is nearly exhausted,
fresh solid has to be added.

(c) Preparation of potassium hydrogen carbonate of stoichiometric composition

Potassium hydrogen carbonate very slowly decomposes upon standing in air, by
losing water and carbon dioxide, potassium carbonate being formed. This latter can
easily be reconverted. The material spread out in a very thin layer is placed in a dis-
sicator vessel filled with carbon dioxide and a small amount of water, where it is stored
for 1–2 days. Upon the action of carbon dioxide and water vapour, the potassium car-
bonate is retransformed into potassium hydrogen carbonate, which loses its adhesive
humidity in several hours in air.

It is expedient to determine the titre of the hydrochloric acid solution by using as
standard the very same pretreated potassium hydrogen carbonate.

(d) Preparation of carbonate-free sodium hydroxide according to Kolthoff

45 g NaOH is dissolved in 500 ml distilled water. 30 g CaO is slaked with a small
amount of water and added to the NaOH solution, which is then made up with water

to 1000 ml. After storage for 1−2 days, the calcium carbonate will be precipitated. On tenfold dilution of the clear solution, 0.1 N sodium hydroxide solution is obtained. This solution is carbonate-free, but contains about 2 mg l^{-1} $Ca(OH)_2$, which causes practically no disturbance.

(e) Titre of a sodium hydroxide solution under various conditions

As examples, Table 1 shows the titres of sodium hydroxide solution containing a small amount of carbonate, determined in different ways.

The titres were determined in the conventional way; the base was titrated with acid (t_I, t_{II}, t_{III}) and conversely, the acid was titrated with base (t_{IV}, t_V) against methyl red + methylene blue (t_I, t_{IV}) and phenolphthalein, respectively, as indicators; titration was performed up to a colour change (t_{II}, t_V); and titration was performed after repeated boiling in order to expel carbon dioxide (t_{III}).

For better orientation, the value of the measured titre was modified to exactly $t_I = 1.0000$, while the values of the other titres were changed proportionately.

(f) Selection of the reference material

Powdery aluminium oxide ignited at 1500° and used in general as reference material still has a large active inner surface area and so it may react with the decomposition product sulphur trioxide and bind a significant amount of it (Part IV of the publication). Therefore, either corundum powder sintered at 1700° or silica powder is used as inert material.

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References

1 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examinations by Means of the Derivatograph, vol. XII. Part A., in series Wilson and Wilson's Comprehensive Analytical Chemistry ed. G. Svehla advisory ed. W. W. Wendlandt. Elsevier, Sci. Pub. Comp. Amsterdam, 1981.

2 J. Paulik and F. Paulik, Mikrochim. Acta, (1966) 886.

3 J. Paulik and F. Paulik, Thermochim. Ac.., 3 (1971) 13.

4 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 25 (1982) 327.

5 J. Paulik, F. Paulik and M. Arnold, Therm Analysis, Proc. Int. Conf. 1982, Kingston Wiley Heyden Chichester, 1982, vol 1 p. 621.

Zusammenfassung — Es wird die gas-titrimetrische (TGT) Einheit einer Apparatur für gleichzeitige TG, DTG, DTA und EGA (Derivatograph) beschrieben. Detaillierte Informationen über die zur Ausführung genauer und reproduzierbarer Ergebnisse anzuwendenden experimentellen Bedingungen werden gegeben.

Резюме — В статье приводится описание термогазотитриметрической приставки для совмещенных ТГ—ДТГ—ДТА—АВГ методов. Приведена подробная информация об экспериментальных условиях, используемых для получения точных и воспроизводимых результатов.