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DETERMINATION OF NITRATE CONTENT OF METAL NITRATES BY MEANS OF SIMULTANEOUS TG, DTG, DTA AND EGA

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INTRODUCTION

In the course of the past two decades thermo-gas-titrimety /TGT/ has promoted the solution of many research problems [1]. This technique [2,3] belongs actually to the evolved gas analytical (EGA) methods. With the help of TGT technique the amount of many gaseous decomposition products (CO_2, CO, SO_2, SO_3, HCl, Cl_2, NH_3, NH_4Cl etc) can be determined independently of the other parallel liberated gaseous products. Now, we developed a measuring technique for the determination of nitrogen oxides (NO_2, NO), too.

FUNDAMENTAL PRINCIPLES OF THE DETERMINATION

The determination is based on the fact that in the course of the decomposition of metal nitrates only NO_2, NO and O_2 would evolve. E.g.:

$$Ca(NO_3)_2 = CaO + NO_2 + O_2 \qquad (1)$$

NO_2 and NO can be let absorbed in water and in the presence of oxidizing agents (H_2O_2) can be transformed into nitric acid which in pH-stat manner can continuously be titrated with NaOH solution by means of an automatic burette.

N_2O_3, N_2O_4, N_2O_5 can also be transformed into nitric acid. According to experience if the examination is carried out in oxygen atmosphere, then N_2 and N_2O gases will be formed only in trace amounts.

APPARATUS AND ITS OPERATION PRINCIPLE

By means of the Derivatograph (produced by the Hungarian Optical Works, MOM, Budapest) shown in Fig. 1 the weight change of the sample (TG), the rate of the weight change (DTG), the rate of the enthalpy change (DTA) as well as the amount and course of the gaseous products liberated from the sample (TGT) and rate of this process (DTGT) can simultaneously be measured.

The decomposition products liberated from the sample, in the present case $NO_2 + NO + O_2$ are quantitatively collected in the

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inside of the corundum bell (4) and conducted by means of O_2 as carrier gas and some wash-water through a capillary tube (24) into the first absorber vessel (25). Here the gas mixture is bubbled through water which contains also H_2O_2. The water absorbs the NO_2, whereupon immediately HNO_3 is being formed. Thereafter pH of the solution changes what is sensed by a glass (35) and calomel (34) electrode couple and by the mV-meter (36) connected into the circuit. Into this latter a control device is incorporated which operates the automatic burette (37,38,39) as soon as the absorption solution reaches the pH value selected in advance (pH=4.5). This adds so rapidly and so much titrant (NaOH solution) to the first absorption vessel (25) that between the two pH values practically no difference should exist (pH stat titration) The piston (39) of the automatic burette actuates also the slide (41) of a potentiometer (40). The signals of the potentiometer fixed by means of a recorder (42) yield the TGT curve while with previous deriving (44) of this one the DTGT curve is obtained. Since the absorption of the gaseous decomposition products occurs in the first absorption vessel (25) not in a quantitative way (table 1.) therefore a second absorption vessel (27) was applied too. This solution was made alkaline in order to promote the binding of NO_2. Finally the excess of the NaOH was titrated with HCl titrant back, and by calculating the results the amount of the consumed NaOH was taken into correction.

DISCUSSION

The model experiments were performed with $Ca(NO_3)_2$. This metal nitrate can viz. be prepared with stoichiometric composition. The analysis of the data contained in table 1 shows that the described method is suitable for the determination of the nitrate content of metal nitrates.

Although according to the data of the table on the average only 98.5 % of $Ca(NO_3)_2$ could be measured under the given conditions the methodical error (-1.5 %) was well reproducible, which analogous to correction methods widely used in classical analysis, can be taken into account. It is to be noted that the magnitude of this methodical error may change in a small extent in dependence of the applied apparatus, the experimental conditions and the compounds investigated, too. Therefore, the equipment should be calibrated one times by a series of measurements. Thereafter in the knowledge of the methodical error the measurements are to be carried out strictly under the previously fixed conditions and the obtained results should be corrected with this value. In this way the accuracy of the measurements will be influenced only by the accidental error (columns 5-6 in table 1).

From the point of view of accuracy and reliability of the method it is to be taken into consideration that our primary aim was not to develop a new analytical method for the determination of the nitrogen content but to elaborate a measuring technique by means of which the single elementary decomposition process of metal nitrates and nitrites, resp. can selectively be followed and so in general the mechanism of thermal reactions can be studied. Such an example will be demonstrated in the instance of the decomposition of $AgNO_3$ in the second part of our paper [5].

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Table 1

measured N_2O_5					
in absorber vessel			mean	deviation	standard deviation
I	II	I+II			
1	2	3	4	5	6
%					
94.4	5.3	99.7	98.5	+1.2	± 0.7
93.7	5.7	99.4		+0.9	
91.5	7.0	98.5		0	
93.0	4.7	97.7		-0.8	
91.2	7.2	98.4		-0.1	
92.3	6.5	98.8		+0.3	
90.1	8.8	98.9		+0.4	
91.1	8.1	99.2		+0.7	
90.1	7.9	98.0		-0.5	
88.3	9.1	97.4		-1.1	
90.9	6.9	97.8		-0.7	

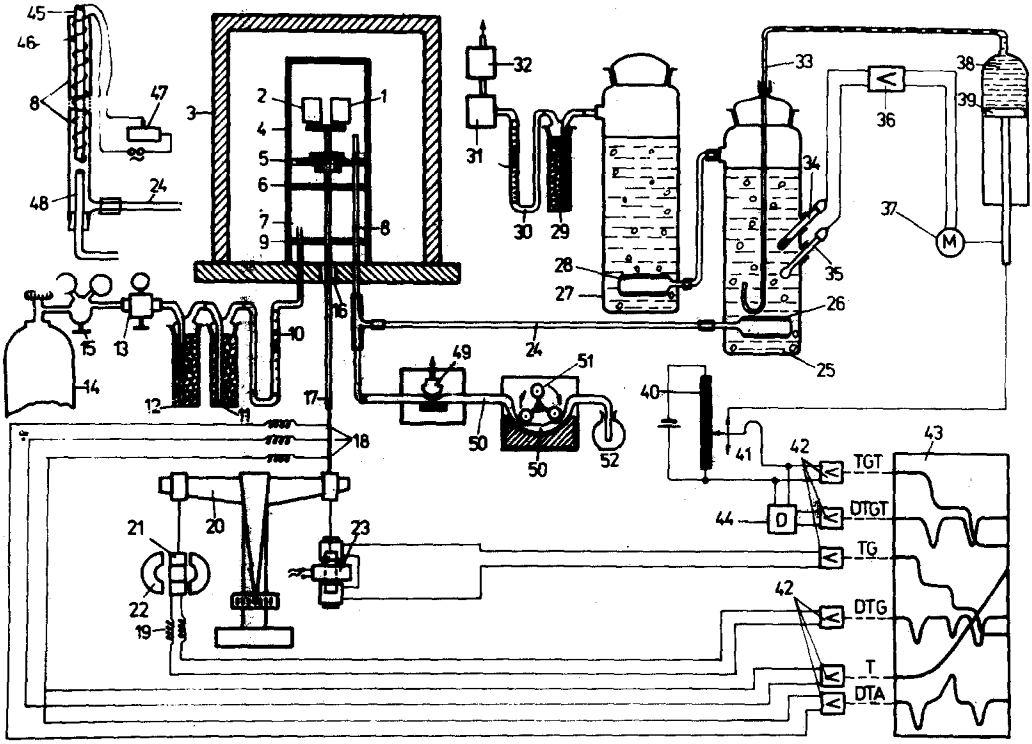

Fig.1 DERIVATOGRAPH FOR SIMULTANEOUS TG DTG DTA AND EGA

1. crucible for the sample; 2. crucible for the reference material; 3. electric furnace; 4. corundum bell; 5. upper corundum diaphragm disc to realize a gas-trap; 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 asbestes (ascarite) for gas purification; 13. governer 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;I; 26. glass filters; 27. absorption vessel II; 28. glass filters; 29. bottle filled with silica gel for gas drying; 30. gas flow meter; 31. control unit for gas flow; 32. vacuum pump; 33. inlet tube for the titrant; 34. reference calomel electrode; 35. glass electrode; 36.pH-meter switch; 37. servomotor of the automatic burette; 38.cylinder of the automatic burette; 39. piston of the automatic burette; 40. potentiometer; 41. sliding of the potentiometer; 42. pens of the recorder; 43. chart of the recorder; 44. deriving device.