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Thermometry, enthalpimetry

A NEW EQUIPMENT BASED ON THE INVERSE-DIE METHOD

Application of a twin-calorimeter in agricultural industry I.

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An automated twin-calorimeter has been developed for the analysis of relatively small sample series which is suitable for the simple and fast analysis of fertilizers. The apparatus was given the name AGROTHERM

Direct injection enthalpimetry (DIE) is a technique [1] in which the reagent of strictly the same heat capacity (C_R) is added in excess and in one portion to the dilute sample solution of large volume with constant heat capacity (C_S) contained in the calorimeter vessel. The volume of the reagent is about one order of magnitude smaller, its concentration one or two orders of magnitude higher than that of the sample solution. Measurements are separate.

In the inverse-DIE technique [2] a large volume of the concentrated reagent solution (heat capacity C_R) is contained in the calorimeter vessel, and small volume samples (heat capacity C_S) are introduced into the reagent solution in series until the course of reaction and the sum of the heat capacity $C_S + C_R$ remain unchanged. Constant volume is ensured by a syphon [3]. After the reaction has completed with the previous sample, a solution portion equal in volume to sample is removed by the syphon before the next sample is introduced.

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Description of the twin-calorimeter AGROTHERM

The above technique has been further developed using the so-called twin-principle: there are two measuring cells of similar shape, both containing reagent solution of equal volume and concentration. Both vessels contain a thermistor and the two thermistors are counter-connected. The sample solution is introduced into one of calorimeters, and simultaneously a reference solution prepared according to the standard method into the other one from two small holders of equal volume. The signal observed after the reaction has proceeded is proportional to the temperature difference of the two calorimeters, and to the difference of the concentration of the sample from that of the reference solution.

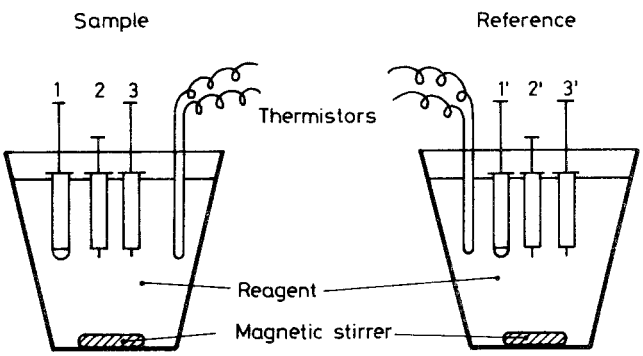

Fig. 1 Scheme of the measuring space of the twin calorimeter 1, 1′ solutions in the syringe; 2, 2′ solutions introduced into the reagent; 3, 3′ reaction mixture sucked back into the syringe

After the reaction has taken place, a portion of the solution in both calorimeters is sucked back into the sample holders in order to keep the volume and the heat capacity of the solutions in the calorimeters constant (the liquid level rises only slightly, a few hundredth of a millimeter after sample addition, which returns to the original level after the back-suction).

As a sample holder a so-called "insulin" syringe available commercially can be used. It can be closed by the cap of the plastic protecting sleeve of the needle. Thus any mixing is avoided and isothermal conditions are ensured.

If the concentration of the sample solution is equal to that of the reference solution, there is no signal on the recorder trace. If the sample is more concentrated than the reference solution of prescribed concentration and the reaction is exothermic, the signal is as shown by curve 2, 2′.

If the sample concentration is lower than the reference concentration, the recorder trace is like curve 3, 3'.

Usual reagent volume: 100–200 ml; sample volume: 1–2 ml. 6 syringes are accommodated in the measuring head.

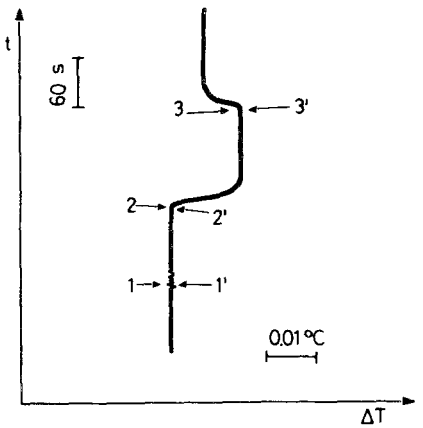

Fig. 2 Recorder trace of AGROTHERM

The measurement may be programmed. The results can be recorded and/or printed. The twin-calorimeter can be operated in the difference mode as described, but the two calorimeters may be used separately. After a calibration in a programmed mode 3 parallel measurements can be made on 4 samples, or 1 measurement on 12 samples, according to the precision required.

The two calorimeters are situated in a single bed, and as many pairs of calorimeter can be used as in the number of components to be determined. A specific pair of calorimeters containing the reagents during the analysis time of the other components may be set aside and then used again.

The application of AGROTHERM is demonstrated by the analysis of multicomponent suspension fertilizers which have been used in increasing amounts in Hungary during the past ten years. At present 400 thousand tons are produced yearly by thirty regional mixing stations. The production is expected to increase to five-fold to the end of the century. The production is discontinuous. A maximum of 6 charges are produced in a shift, and each charge has to be analysed. The reagents used in the determinations by AGROTHERM are prepared so that one portion of reagent in the calorimeter is enough for 3 parallel determination per charge per shift and with a good utilization of the reagent.

Thus the requirements are in accordance with the performance of the apparatus.

References

1 I. Sajó, Termometria, Műszaki Könyvkiadó, Budapest 1971.
2 P. Marik-Korda, J. Thermal Anal., 13 (1978) 357.
3 Hung. Pat. 190484 (1985).

Zusammenfassung — Es wurde ein für quantitative thermometrische Messungen geeignetes Zwitterkalorimeter entwickelt. In zwei Kalorimetern gleicher Bauweise wird gleichermassen präpariertes Reagenz placiert, von welchen in das eine die Probenlösung, in das andere die in einem Standardverfahren präparierte Bezugslösung dosiert wird. Zwei in einer Wheatstonschen Brücke gegenübergeschaltene Thermistoren liefern ein der Konzentrationsdifferenz beider Lösungen proportionales Signal. In beide Kalorimeter tauchen jeweils 6 Probenbehälter gleichen Volumens. In Abhängigkeit von der Reaktionsgeschwindigkeit kann deren Inhalt nacheinander in gleichen Zeitabständen in das Reagenz dosiert werden, wodurch die Messung kleiner Serien möglich wird.

Резюме — Разработана двухкалориметрическая система пригодная для термометрических (калориметрических) количественных определений. В два совершенно одинаковых калориметра помещали реагепт, приготовленный одним и тем же способом. В один из калориметров прибавляли раствор исследуемого образца, а во второй — раствор сравнения, приготовленный стандартным способом. Два термистора, соединенные друг против друга в мостике Уинстона, выдают сигнал, пропорциональный разнице концентраций двух растворов. В оба калориметра погружают 6–6 одинаковых по объему образцов, содержание которых в одинаковые интервалы времени, в зависимости от скорости реакции, последовательно прибавляют к реагенту. Таким образом, представляется возможность измерять небольшие серии образцов.