# AN INVERSE DIE METHOD

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The inverse of the usual DIE method is presented. The solid or liquid samples are introduced successively into the reagent of high concentration and large volume, and the change in temperature is measured after each sample. In principle the measuring unit need not be opened until the reagent is exhausted. The new technique is rapid and economical.

The amount of product formed in a chemical reaction is determined by that of the reactant initially present in stoichiometrically smallest amount. The heat formed and (under adiabatic conditions) the temperature change $\Delta T$ will be proportional to the latter.

This phenomenon is utilized for chemical analysis or thermometric analysis, e.g. in direct injection enthalpimetry (DIE) [1].

$$\left.\begin{aligned} Q &= n\Delta H \\ Q &= C\Delta T \end{aligned}\right\} \quad \Delta T = n\frac{\Delta H}{C}$$

where

$Q$ is the amount of heat formed (cal),
$n$ is the number of moles of sample,
$\Delta H$ is the molar heat of reaction (cal/mole),
$C$ is the heat capacity of the system (cal/°),
$\Delta T$ is the temperature change observed (°).

For the temperature change to be proportional to the amount of sample, the ratio $\frac{\Delta H}{C}$ should remain constant. The condition for this is to measure small temperature changes at practically constant temperature.

The usual procedure for the determination is as follows: A constant, relatively large volume of the dilute sample solution is contained in the adiabatic measuring unit, and a constant small volume of the concentrated reagent in the immersion pipette. After thermal equilibrium has been established, the reagent is added to the sample.

The measuring unit has to be opened after each determination, the reacted

sample removed and the new sample introduced. The measurement can be started only after thermal equilibrium has been established again (10 to 15 min).

This technique has been modified for the purpose of determining the active component in some solid substances (e.g. medicine tablets) so that the sample was added to the reagent contained in the measuring unit [2, 3]. The measurement became faster, and in some cases more suited to the purpose.

The modified method is especially worth using if the samples are of small and practically equal weights (e.g. medicine tablets, which may be hygroscopic or may tend to decompose). The constancy of the heat capacity is thus ensured.

If only a small amount of sample is available, and the heat of reaction is large, an even simpler and more economical means of determination presents itself: a large volume of concentrated reagent is taken in the measuring unit and the samples can be added in succession as long as the reaction proceeds in the same way and the heat capacity remains practically constant.

In this way we succeeded in determining water in organic solvents, using Karl Fischer solution as reagent [4]. The reagent could be used until complete exhaustion, that is, the concentration of the reagent did not affect the temperature changes observed, which means that the specific heat, density and ionic strength remained practically constant, as the introduction of successive sample portions (some drops each time) did not alter the relatively large basic heat capacity.

The two methods can be combined so that tablets are added in succession to a large volume of concentrated reagent. To illustrate the new method the determination of hydrogen peroxide in "Hyperol" tablets is presented.

## Experimental

*Apparatus:* MOM Directhermon (Fig. 1)

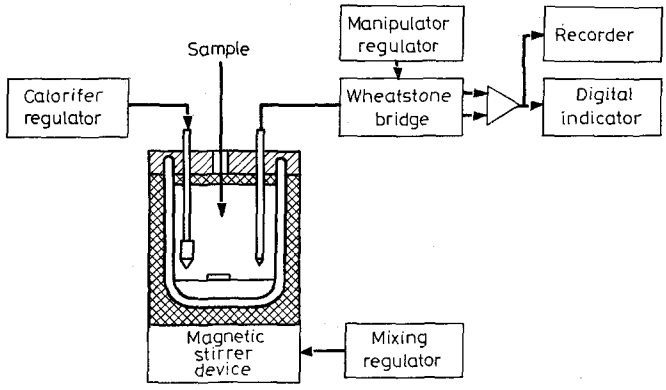


Fig. 1. Block diagram of Directhermom (without immersion pipette)

*Reagents:*

20% KI solution
10% HCl solution
1*M* $(NH_4)_2MoO_4$ solution
"Hyperol" tablets (nominal composition: 33–36% $H_2O_2$ + urea)

*Preparation of a calibration graph*

100 ml 20% potassium iodide and 100 ml 10% hydrochlorid acid were added to the sample holder at room temperature. After thermal equilibrium had been established, different parts of known weight (10 to 70 mg) of a 1 g tablet were added, and the scale deflection was recorded after each addition (full-scale deflection: 50 mV, corresponding to $\Delta T \simeq 0.2°$). After 15–20 measurements, in which the whole tablet was consumed, the sample holder was taken out of the measuring unit and the iodine produced was titrated with standard sodium thiosulphate solution.

The series of measurements was repeated using portions of a powdered tablet, and also in the presence of a few drops of molybdate catalyst solution.

A blank test was carried out with urea, the stabilizer of hydrogen peroxide in the tablet, which is at the same time the excipient of peroxide.

200 ml reagent was mixed under air for 8 hours, and the iodine produced was titrated.

The hydrogen peroxide was determined in the "Hyperol" tablet according to the Pharmacopoeia Hungarica, Ed. VI.

Further, 15 measurements were carried out on 40–60 mg samples in order to calculate the standard deviation.

## Results and discussion

The galvanometer deflection was plotted against the amount of hydrogen peroxide in the sample. The plot was a straight line both when small particles of the tablet and when powdered portions of the tablet were used (Fig. 2).

The equation of the calibration curve was calculated by least-squares analysis.

$$y = -1.1 + 1.3\,x$$

where $y$ is the scale deflection (division) and $x$ is the amount of hydrogen peroxide (mg).

The standard deviation was calculated from 15 parallel measurements using the equation

$$S = \pm \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$

where

$x_i - x$ is the deviation of single values from the mean,
and $x_i$ is the specific scale deflection (division/mg $H_2O_2$)

The standard deviation was found from 15 determinations to be

$$S = \pm 0.100 \text{ scale defl./mg } H_2O_2$$

From the result of the titration with sodium thiosulphate

a) we could see whether or not the amount of peroxide prescribed was present in one tablet,

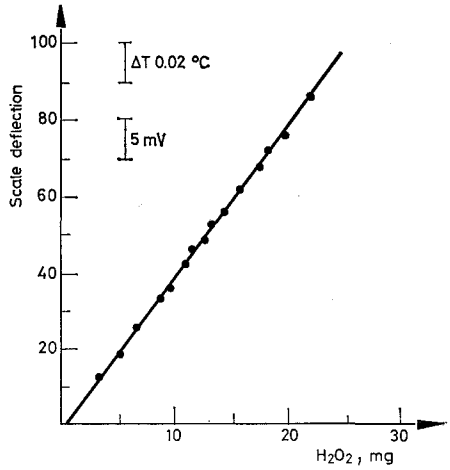


Fig. 2. Calibration curve of $H_2O_2$ (recorder scale-deflection as a function of the $H_2O_2$ content of the Hyperol tablet)

b) we could calculate the amount of potassium iodide consumed.

0.25% of the reagent was found to undergo oxidation during 8 hr mixing under air. In principle, this could result in a base-line shift and should be taken into consideration when calculating the result. However, the base-line shift is so small during the time of a measurement that it can be neglected.

The amount of hydrogen peroxide found to be present in one tablet by iodometric titration corresponds to that prescribed in the Pharmacopoeia Hungarica, Ed. VI.

Only 10% of the potassium iodide was consumed in 15–20 measurements. Further measurements can be performed in the solution as long as the residual potassium iodide is enough to keep the iodine liberated in solution.

Summing up, one can conclude that

a) the reaction is instantaneous if potassium iodide is present in a great excess;

b) the reaction rate decreases as the excess of potassium iodide decreases, but this adverse effect can be eliminated by using molybdate as catalyst;

c) the calibration curve starts practically from the origin, which means that the excipient is inert; this was also supported by experimental evidence;

d) the concentration, or the change in the concentration of the potassium iodide used does not influence the heat capacity of the system, that is, the temperature change observed was proportional to the amount of heat formed in each case. Thus, the reagent can be used until exhaustion.

In addition to economicalness, speed is the main advantage of this technique. Measurements can be carried out at intervals of one minute.

If the excipient of the tablet is inert and the material is readily soluble, the method is well suited to compare single tablets, and to test materials which tend to decompose.

The most important thing about the new inverse DIE method is that it enables an apparatus basically designed for analysis of large samples to be used as a micromethod by a simple technical trick.

## References

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RÉSUMÉ — La publication présente une méthode inverse de celle de DIE utilisée de coutume. On introduit les prélèvements solides ou liquides un à un dans le réactif de forte concentration et de grand volume et on effectue la mesure des variations de température après chaque prélèvement. En principe, il n'est pas nécessaire d'ouvrir l'unité de mesure avant que le réactif ne soit épuisé. La nouvelle technique est rapide et économique.

ZUSAMMENFASSUNG — Ein Inversverfahren der üblichen DIE-Methode wird beschrieben. Die festen oder flüssigen Proben werden der Reihe nach in das hochkonzentrierte Reagenz von großem Volumen eingeführt und die Temperaturänderungen nach jeder Probe gemessen. Im Prinzip muß die Messeinheit bis zur Erschöpfung des Reagenzes nicht geöffnet werden. Das neue Verfahren ist schnell und wirtschaftlich.

Резюме — В статье представлен метод, обратный обычному методу ДИЕ. Твердые или жидкие образцы вводились впоследствии в реагент высокой концентрации и большого объёма, а изменение температуры измеряли после каждого образца. В принципе не требуется, чтобы измерительная ячейка была открыта до тех пор пока реагент не исчерпается. Новая техника быстрая и экономичная.