

## A NEW MODIFICATION OF THE INJECTION ENTHALPIMETRY METHOD

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A new modification of the rapid enthalpimetric determination of inorganic and organic substances was developed, based on the measurement of the heat of reaction using an excess of the reagent. Two successive injections of the reagent are applied in order to eliminate the effect of different initial temperatures of the two solutions. The theoretical analysis of the method is given and a simplified measuring equipment is developed. The method is generally applicable to any laboratory or industrial analysis and can be automatized. The duration of one complete analysis including the scanning of the curve is usually lower than 3 minutes.

In an adiabatic system of a constant heat capacity, the heat of reaction causes a change of the temperature of the system ( $\Delta T$ ), proportional to that heat of reaction and thus to the mass amount of the product formed. For reactions whose chemical equilibrium is shifted in favour of the reaction product, a simple relation can be derived between the temperature change of the system,  $\Delta T$ , and the mass amount of any of the initial reactants<sup>1</sup>.

For the reaction



we have the heat balance

$$-Q = n_C \cdot \Delta H_r, \quad (1)$$

where  $n_C$  is the mass amount of the product C,  $\Delta H_r$  the reaction enthalpy per 1 mol of the product, and  $Q$  the total heat of reaction.

The value of  $n_C$  can be related to the mass amounts  $n_A$  and  $n_B$  of the initial reactant A and B, resp., by

$$n_C = (c/a) n_A = (c/b) n_B. \quad (2)$$

Substitution in Eq. (1) leads to

$$-Q = n_A (c/a) \Delta H_r = k n_A. \quad (3)$$

Furthermore, we have

$$\Delta T = Q/C = (k/C) n_A = k' n_A, \quad (4)$$

where  $C$  is the overall heat capacity of the system, and  $k$  and  $k'$  are constants.

From Eq. (4) it follows that  $\Delta T$  is directly proportional to the amount of the substance A entering the reaction (A) and thus to the initial concentration of the substance determined. The reaction can proceed quantitatively only in the presence of the at least stoichiometric amount of the substance B.

The relation (4) holds only if the temperature of the reagent injected equals that of the solution analyzed and if the heats of dilution are zero. Sajo<sup>2</sup> solved the problem of equalization of the temperatures by submerging the reagent, placed in a pipette, into the analyzed solution. He added inert substances to the reagent for the resultant heat of dilution to be zero.

Wasilewski and coworkers<sup>1</sup> have introduced the method of calibration curve. Under the assumptions of zero heat of dilution, a constant difference between the temperature of the reagent and that of the sample, and a constant volume of the reagent added, they derived the following relation for  $\Delta T$ :

$$\Delta T = k'n_A + Q'/C, \quad (5)$$

where  $Q'$  is the heat contributed by the reagent. The intercept of the linear dependence of the heat of reaction on the concentration of the sample is zero if the temperature of the reagent equals that of the sample, positive if the former is higher than the latter, and negative in the opposite case.

Thus the two methods work under the assumptions that the temperature of the sample equals that of the reagent<sup>2</sup> or at least that their difference is constant<sup>1</sup>. In practice, however, these requirements cannot be always satisfied; in fact, it is difficult to estimate the time, after which the temperatures of the solutions are equalized to a degree required for a sufficient satisfaction of these assumptions. Moreover, this satisfaction is problematic in analyses of diluted and very diluted solutions, where  $\Delta T$  is 0.01–0.001°C. We have therefore developed a novel method, which does not require the temperatures of the reagent and of the sample to be equal.

## THEORETICAL

In the method, which we denote "the method of double injection", the reagent is injected successively twice by an injection equipment, which can reproducibly supply small volumes of a solution. On the first injection the whole amount of the component determined reacts with the reagent supplied in excess. The temperature change measured,  $\Delta T'$ , corresponds to the heat of reaction, the heat contributed by the reagent (due to its different temperature), and the heat of dilution of the reagent and of the sample. The second injection brings about a temperature change  $\Delta T''$  accounted for by the difference of temperatures of the reagent and the reaction mixture, and by the heat of dilution. In the difference of the two temperature changes,  $\Delta T = \Delta T' - \Delta T''$ , the interfering effects are compensated to a high extent and the value  $\Delta T$  corresponds to the net heat of reaction.

The heats of dilution accompanying the first and the second injections are not exactly the same, since during the second injection the reagent is added to a medium qualitatively different from that of the first injection. This difference of the two heats of dilution is reproducible and can be taken into account in a calibration curve, which does not then pass the origin, but is shifted on the axis of  $\Delta T$ . Although a similar effect of different temperatures of the sample and the reagent on the shape

of the calibration curve can be supposed, it was found to be practically negligible. Also the compensation of the heats of dilution can be sometimes improved by an appropriate experimental arrangement. Thus, *e.g.*, a sufficient enhancement of the ionic strength of the solution prior to analysis brings about the equalization of the heats of dilution accompanying the two injections. The magnitude of these errors can be determined by calculation.

The total heat  $Q'$  evolved on the first injection of the reagent (B) into the solution of the sample (A) in the reaction vessel (leading to the reaction product C) is given by

$$Q' = -n_A \Delta H_r - n_A \Delta H_A - n'_B \Delta H'_B + Q'_{dT} + Q'_i, \quad (6)$$

that evolved on the second injection is given by

$$Q'' = -n_C \Delta H_C - n''_B \Delta H_B + Q''_{dT} + Q''_i, \quad (7)$$

where  $\Delta H_A$ ,  $\Delta H_B$ , and  $\Delta H_C$  are the changes of enthalpies of one mole of the sample, the reagent, and the reaction product, respectively, accounted for by the dilution on the first ( $\Delta H_A$ ,  $\Delta H'_B$ ) and the second ( $\Delta H''_B$ ,  $\Delta H_C$ ) injection,  $Q'_{dT}$  and  $Q''_{dT}$  are the heats brought into the calorimetric system in consequence of different temperature of the reagent and the sample, and  $Q'_i$  and  $Q''_i$  represent the sums of the other heat effects, *i.e.* the heat contributed by the stirrer and the thermistor and heat losses in the surroundings. The coefficients in the scheme (A) are here put equal to one for the sake of simplicity ( $a = b = c = 1$ ). The superscripts ' and '' denote quantities referring to the first and the second injections, respectively. The quantities  $Q'_i$  and  $Q''_i$  are time-dependent and can be eliminated during the graphical evaluation of the enthalpogram in the usual manner. Subtracting the two heat values we obtain

$$Q' - Q'' = -n_A \Delta H_r - n_A \Delta H_A + n_C \Delta H_C + (n''_B \Delta H''_B - n'_B \Delta H'_B) + (Q'_{dT} - Q''_{dT}). \quad (8)$$

The first three terms on the right side of Eq. (8) are directly proportional to the concentration of the component A in the sample ( $c_A$ ). If the heat capacity of the reagent is assumed to be considerably lower than the total capacity of the system C, and if the magnitude of the two last binomials in Eq. (8) is negligible, then the difference of the temperature changes for the two injections,  $(Q' - Q'')/C$ , is directly proportional to  $n_A$  and thus to the concentration  $c_A$ . The error, which can be introduced in the method with one standard solution, depends on the two last binomials in Eq. (8), the value of which is not proportional to the concentration of the determined component in the sample solution.

We shall now calculate the value of the term  $Q'_{dT} - Q''_{dT}$ , *i.e.* the thermal effect accounted for by the different temperatures of the sample and the reagent.

For the first injection,

$$Q'_{dT} = (T_B - T_A) C_B = \Delta T'(C + C_B) - Q_s, \quad (9)$$

where  $T_A$  and  $T_B$  are the temperatures of the sample and the reagent, respectively,  $C_B$  the heat capacity of the reagent,  $\Delta T'$  the temperature change accompanying the first injection, and  $Q_s$  the sum of other thermal effects (heat of reaction, heats of dilution *etc.*).

For the second injection,

$$Q''_{dT} = (T_B - T_A - \Delta T' - \bar{T} \Delta \tau) C_B, \quad (10)$$

where  $\bar{T}$  is the average temperature trend ( $dT/d\tau$ ) during the time span,  $\Delta \tau$ , between the two injections. We assume the temperature of the reagent to be close to that of the surroundings, so that it does not change appreciably during the time  $\Delta \tau$ . Subtracting Eq. (9) and Eq. (10) and expressing  $\Delta T'$  from Eq. (9) we obtain

$$\begin{aligned} Q'_{dT} - Q''_{dT} &= C_B(\Delta T' + \bar{T} \Delta \tau) = \\ &= C_B\{[(T_B - T_A) C_B + Q_s]/(C + C_B) + \bar{T} \Delta \tau\}. \end{aligned} \quad (11)$$

The term  $Q_s$  does not practically disturb the direct proportionality of the concentration dependence of  $(Q' - Q'')$ , and therefore the absolute error  $\varepsilon_{dT}$  can be expressed as

$$\varepsilon_{dT} = C_B^2(T_B - T_A)/(C + C_B) + C_B \bar{T} \Delta \tau. \quad (12)$$

The relative error with respect to the heat of reaction is then

$$-\varepsilon_{dT}/n_A \Delta H_r \approx (C_B/C)^2 (T_B - T_A)/\Delta T + (C_B/C) \bar{T} \Delta \tau/\Delta T, \quad (13)$$

where  $\Delta T = \Delta T' - \Delta T''$  is the difference of the temperature changes for the two injections. For the sake of simplicity,  $C_B$  was neglected with respect to  $C$  and it is assumed that  $-n_A \Delta H_r \approx C \Delta T$ . In fact,  $C_B/C$  is usually lower than 0.02. Then for the maximum error due to the initial difference between the temperature of the reagent and that of the sample to be, *e.g.*, 1%, it is — according to Eq. (13) — sufficient that  $|T_A - T_B| \leq 25|\Delta T|$ , *i.e.* the difference of the temperatures of the two solutions is allowed to be 25-times higher than the measured temperature difference  $\Delta T$ . The second term in the relation (13), which expresses the relative error caused by the change of temperature due to the temperature trend between two injections, leads in the same case to the condition that  $|\bar{T} \Delta \tau|$  be lower than  $0.5|\Delta T|$ . This condition can be satisfied experimentally very well by making the time span between the two injections as short as possible, or — in critical cases (very slow reaction rate) — by attaining a stationary heat flow through the walls of the reaction vessel before the first injection. The value  $\bar{T} \Delta \tau/\Delta T$  is then minimum.

On the other hand, in the method of one injection the relative error would be

$$Q'_{dT}/C \Delta T' = (C_B/C) (T_A - T_B)/\Delta T' \quad (14)$$

and for a 1% error the two solutions would have to be temperature-balanced so that the temperature difference  $|T_A - T_B|$  not exceed  $0.5 |\Delta T'|$ ; this can be rather difficult to satisfy if the  $\Delta T'$  value is very low.

Now, the maximum "error" due to dilution of the reagent B during the two injections, *i.e.* the magnitude of the difference  $(n''_B \Delta H''_B - n'_B \Delta H'_B)$  in Eq. (8) will be estimated for the case, when the solution contains only the component determined (A) and the solvent. For the first injection the enthalpy change is

$$n'_B \Delta H'_B = n_B(\Delta H(n_1) - \Delta H(n_0)), \quad (15)$$

where  $\Delta H(n_0)$  and  $\Delta H(n_1)$  are the integral molar heats of dilution for the infinite dilution of one mol of the reagent B,  $n_0 = (1000\rho_B - c_B M_B)/M_S c_B$  is the mass amount of the solvent per one mol of the substance B in the reagent,  $n_1 = (1000\rho_A V_A + 1000\rho_B V_B - n_B M_B)/M_S n_B$  is the same quantity in the reaction solution on the first injection (before the reaction),  $\rho_A$  and  $\rho_B$  are the densities of the sample and of the reagent, respectively,  $M_B$  and  $M_S$  are the molecular weights of the reagent B and of the solvent, respectively,  $c_B$  is the molar concentration of the reagent B, and  $V_A$  and  $V_B$  are the volumes of the sample and the reagent, respectively. Now we shall again treat the simple case, where  $a = b = c = 1$ . The values  $\Delta H(n_1)$  and  $\Delta H(n_0)$  can be substituted in Eq. (15) by the corresponding integral heats of dissolution with the opposite signs.

Analogously, for the second injection we have

$$n''_B \Delta H''_B = (2n_B - n_A) \Delta H(n_2) - (n_B - n_A) \Delta H(n'_1) - n_B \Delta H(n_0), \quad (16)$$

where  $n_2 = [1000\rho_A V_A + 2(1000\rho_B V_B - n_B M_B)]/(2n_B - n_A) M_S$  is the mass amount of the solvent per one mol of the reagent B in the reaction solution after the second injection and  $n'_1 = n_1 n_B / (n_B - n_A)$  is the same quantity before the second injection (after the reaction). By subtracting Eq. (15) from Eq. (16) we obtain the general formula for the absolute error  $\varepsilon_a$  in the double injection method as follows:

$$\varepsilon_a = (2n_B - n_A) \Delta H(n_2) - (n_B - n_A) \Delta H(n'_1) - n_B \Delta H(n_1). \quad (17)$$

In the case of a high stoichiometric excess of the reagent ( $n_B \gg n_A$ ), Eq. (17) is simplified to

$$\varepsilon_a \approx 2n_B(\Delta H(n_2) - \Delta H(n_1)). \quad (18)$$

The relative error with respect to the heat of reaction is then

$$\begin{aligned} \varepsilon_r &= \varepsilon_a/n_A \Delta H_r \approx \\ &\approx (2c_B V_B/c_A V_A \Delta H_r) (\Delta H(n_2) - \Delta H(n_1)). \end{aligned} \quad (19)$$

Calculate the value of  $\varepsilon_r$  for the acidimetric determination of a strong base with a solution of hydrochloric acid using a ten-fold stoichiometric excess of the reagent. Put  $c_A = 0.01\text{M-NaOH}$ ,  $V_A = 0.020\text{ l}$ ,  $c_B = 1\text{M-HCl}$ ,  $V_B = 0.002\text{ l}$ ,  $\Delta H_r = -1.3 \cdot 10^4\text{ cal mol}^{-1}$ . Then  $n_1 \approx 610$ ,  $n_2 \approx 332$ . The values  $\Delta H(610) \approx -153\text{ cal mol}^{-1}$  and  $\Delta H(332) \approx -198\text{ cal mol}^{-1}$  were found by a graphical interpolation of published data<sup>3</sup>; substituting in Eq. (19) we obtain  $\varepsilon_r = 0.07$ . For the same excess of the reagent and the same dilution ratio,  $\varepsilon_r = 0.10$  and  $0.035$  for  $c_B = 2\text{M-}$  and  $0.1\text{M-HCl}$ , respectively.

### EXPERIMENTAL AND RESULTS

Reagent grade chemicals were used throughout. The solutions were prepared and standardized in the usual manner.

The experimental equipment set up for testing the method of "double injection" comprises — like other discontinuous methods — a Dewar flask, in which is placed a stirrer and the supply of the reagent connected with an injection pipette (syringe 3 ml); the mouth of the supply is placed

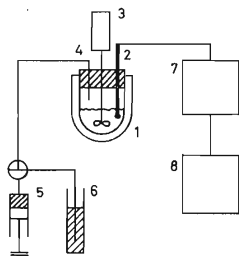


FIG. 1

Scheme of the Apparatus

1 Dewar flask, 2 thermistor, 3 d.c. motor of the stirrer, 4 capillary inlet of the reagent, 5 syringe, 6 reservoir of the reagent solution, 7 Wheatstone bridge, 8 recorder.

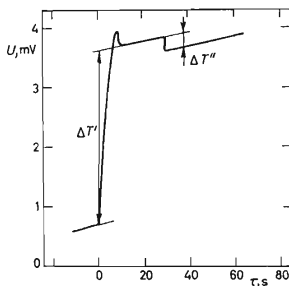


FIG. 2

Schematic Scan of the Temperature During the Determination by the Method of "Double Injection"

$\Delta T'$  and  $\Delta T''$  are the temperature changes accompanying the first and the second injections, respectively.

above the surface of the sample. The temperature of the analyzed filling of the Dewar flask was measured by means of a thermistor resistance thermometer (reference resistance  $R_S$  ( $25^\circ\text{C}$ ) =  $3.6\text{ k}\Omega$ ), connected in a Wheatstone bridge whose output (voltage) is connected to a compensation recorder EZ 4 (Laboratorní přístroje, Prague). The scheme of the equipment is apparent from Fig. 1. The thermistor is linearized by a parallel resistance of  $10\text{ k}\Omega$ . Resistors with a low temperature coefficient of the electric resistance (type TR 162, Tesla, Lanškroun) were used in the bridge.

The method of double injection was tested for various types of chemical reactions, using the method of calibration curve or of one standard. 20 ml of the sample or the standard were pipetted for the determination. The volume of the injection reagent solution was 2–3 ml. The probable deviations (P) were calculated by using the critical values of the Student distribution<sup>4</sup> for a 95% probability (for six determinations); they are listed in Table I for the given concentrations. The reported values of enthalpies of reaction are experimental data, save the heat of the neutralization reaction taken from the book of Brdička<sup>5</sup>. The evaluation of the enthalpogram is apparent from Fig. 2. The weak maximum on the curve appearing just after the first injection is due to the temporary overheating of the thermistor, which occurs sometimes during fast reactions.

In addition to the test of reproducibility of the double injection method, the maximum "error" due to the different dilutions of the reagent B accompanying the two injections (Eq. (19)) was followed as well. The concentration dependence of the heat of reaction was measured for the reaction of neutralization of sodium hydroxide ( $c_A = 0.001, 0.01, \text{ and } 0.02\text{ mol l}^{-1}$ ) with hydrochloric acid ( $c_B = 0.1, 1.0, \text{ and } 2.0\text{ mol l}^{-1}$ , resp.); the extrapolated value of this dependence for  $c_A = 0$  (value  $\epsilon_s$ , Eq. (17)) agrees with the values measured for a sample with zero concentration of NaOH. The values of  $\epsilon_r$ , calculated from the experimental data are 0.02, 0.05, and 0.08 for the above values of  $c_A$  and  $c_B$ .

## DISCUSSION

Table I indicates a relatively good reproducibility of the method (approximately 1%) for five different systems. The values  $\epsilon_r$  for the neutralization reaction between NaOH and HCl are only slightly different from those calculated according to the theory (0.035, 0.07, and 0.10, resp.). This error is the maximum one, because it corresponds to the dilution of the reagent in a solution with a low concentration of the sample,

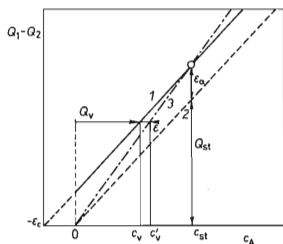


FIG. 3

Graphical Illustration of the Relation Between the Analytical Error and the Error due to the Dilution of the Reagent

1 Heat measured, 2 heat proportional to the concentration of the sample, 3 straight line for the evaluation of the concentration of the sample (for symbols see the text).

TABLE I

Probable Deviations of the Enthalpimetric Determination by the Double Injection Method for Different Types of Reactions

A	B	$c_A$ mol · l <sup>-1</sup>	$c_B$ mol · l <sup>-1</sup>	P %	$\Delta H_r$ kcal mol <sup>-1</sup>
KOH	HCl	0.0200	1	±0.7	-13.75 <sup>a</sup>
KH <sub>2</sub> PO <sub>4</sub>	KOH	0.1070	2	±1.3	-27.2
Fe <sup>2+</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.0510	0.25	±0.5	-25.8
	2M-H <sub>2</sub> SO <sub>4</sub>				
ClO <sup>-</sup>	KI	0.0532	1	±0.75	-27.0
Ca <sup>2+</sup>	Mg-EDTA	0.0193	0.2	±1.0	- 5

<sup>a</sup> Ref.<sup>4</sup>.

while in fact the sample can contain an indifferent electrolyte whose presence causes the enthalpy of the reagent in the reagent solution to approach that in the sample solution (on dilution). Clearly, the heats of dilution of the indifferent electrolyte are here compensated more perfectly than those of the reagent, therefore that case was not treated in the theoretical part. On the other hand, in the method of one injection the presence of the indifferent electrolyte can be a potential source of a relatively high error, especially if the amount of the electrolyte fluctuates.

From the  $\epsilon_r$  values it also follows that — regarding the heat of dilution of the reagent — it is preferable to use a less concentrated solution of the reagent provided that the stoichiometric excess is maintained. The value  $\epsilon_r$  is not a real error in the analytical sense, it merely represents the portion of heat, which is not proportional to the content of the component determined. The relative systematic error in the method of one standard solution can be calculated by means of Fig. 3 (here  $c_{st}$  denotes the concentration of A in the standard,  $c_v$  and  $c'_v$  the actual and the found concentrations of A in the sample, resp.,  $\epsilon$  the absolute error, for  $\epsilon_c$  see Fig. 3,  $Q_{st}$  is the portion of heat proportional to the concentration of A in the standard, and  $Q_v$  the resultant thermal effect occurring during the measurement of the sample). From geometric relations it follows that  $\epsilon_r = \epsilon_a/Q_{st} = \epsilon_c/c_{st} = \epsilon/(c_{st} - c'_v)$ , hence  $\epsilon = \epsilon_r(c_{st} - c'_v)$ ; rearranging and putting  $c'_v \approx c_v$  we obtain the relative systematic error  $\epsilon/c_v \approx \epsilon_r(c_{st}/c_v - 1)$ . Thus the relative systematic error in the determination of the sample is lower than  $\epsilon_r$  (here corresponding to the standard) in the interval of  $c_v \in (0.5c_{st}; \infty)$ , for  $c_v \rightarrow c_{st}$  it approaches zero.

As calculated in the theoretical part, the error  $\epsilon_r$  — and thus also the relative systematic error — in the method of one injection is approximately 3-6-times higher. With regard to the compensation of the heat of dilution, the method of double



injection is suitable particularly if a higher stoichiometric excess of the reagent is required (*e.g.* for reactions, which proceed only slowly if a low excess of the reagent is applied). By the second injection of the reagent we can often avoid the measurements of several standard solutions and the plotting of the calibration curve, which rationalizes the method and facilitates its automation.

An additional improvement can be achieved by the compensation of the effect caused by the different temperatures of the reagent and of the sample. As follows from the theoretical part, for the same error the difference of the temperatures is allowed to be fifty times higher than in the method of one injection, which brings about essential speeding-up of the method, enhancement of its accuracy and precision, and — for the automation — a considerable improvement of its dynamical aspects.

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