

Determination of aromatic amines by the method of direct injection enthalpimetry

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An enthalpimetric determination of aromatic amines based on the diazotization and nitrosation reaction heats has been developed. This determination was verified with seven selected amines, *i.e.* sulfanilic acid, *p*-aminobenzoic acid, aniline, *o*-toluidine, α -naphthylamine, benzidine, and diphenylamine. The method of double injection, especially suited for high values of reaction heats was applied.

Было разработано энталпиометрическое определение ароматических аминов, обоснованное на теплоте реакций диазотирования и нитрозирования. Определение было испытано на семи избранных аминах: сульфониловой и *p*-аминобензойной кислотах, анилине, *o*-толуидине, α -нафтил-амине, бензидине и дифениламине. Был использован метод двойного впрыскивания, который подходит особенно в случае высоких теплот реакций.

Many methods founded on oxidation-reduction, acid-base, diazotization, nitrosation, and coupling reactions were developed for the determination of aromatic amines.

The oxidation products of amines may be especially used for photometric determinations [1]. Another way is the oxidation of amines by sodium chlorite and subsequent iodometric determination of excess reagent [2]. This reaction may be also used for photometric determination [3]. The titration of amines with a strong acid in nonaqueous medium also affords good results [4].

Many methods of the determination of aromatic amines are based on the reaction with nitrous acid. The diazotization reactions may be applied to volumetric determination of primary aromatic amines [5]. *Remizov* [6] used the difference in the degree of diazotization for the determination of aromatic amines in mixtures. The titration end-point is to be found visually [5] and still better potentiometrically, amperometrically or biamperometrically [5, 7—9].

Similarly, the nitrosation reactions may be also employed for volumetric determinations [5]. They are useable for secondary amines, but in case of tertiary amines, the reaction proceeds slowly and necessitates specific conditions.

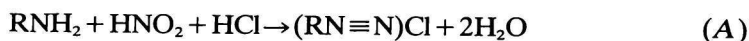
Aliphatic and aromatic amines may be also successfully determined thermometrically by titrating with strong acids, most frequently with perchloric or hydrochloric acid in nonaqueous media. For instance, aliphatic and aromatic amines even in the presence of each other may be determined by titrating with hydrochloric acid in isopropanol [10]. Other authors used the thermometric titration with perchloric or hydrochloric acid in dioxan [11] for the determination of amines and recommended the thermometric titration with perchloric acid in isopropanol or the mixed solvent isopropanol—ethylene glycol for the mixtures of primary, secondary, and tertiary amines. α -Methylstyrene and isobutylethane may be used as media for the thermometric titration of amines [12].

The diazotization reactions, too, were analytically employed for the thermometric titration of aromatic amines. The best results were achieved in the medium of hydrochloric acid and potassium bromide [13].

All this information was examined and, in particular, the diazotization reactions were used for a direct enthalpimetric determination of aromatic amines by means of the method of "double injection" [14—19].

Theoretical analysis of the conditions of determination

Primary aromatic amines are subjected to diazotization which involves the reaction with nitrous acid in the presence of hydrochloric acid



whereas secondary aromatic amines undergo the nitrosation reaction



Nitrous acid arises from sodium nitrite according to the following reaction



Reactions (A), (B), and (C) can be very well applied to the enthalpimetric determination of the above amines by using the method of double injection. That results from the approximate values of molar reaction heats which were measured and calculated on the basis of the slopes of calibration curves and of the comparison with the data obtained from the neutralization reaction of sodium hydroxide with hydrochloric acid with the known value of molar reaction heat. The results of measurements are in good agreement with the values published by other authors [13].

For the proper determination of aromatic amines, it is very important to know the convenient concentration of hydrochloric acid because it significantly influ-

ences the error of measurement. For illustration, the concentration dependence of the error of measurement and of the value obtained in blank assay at the determination of sulfanilic acid is given in Table 1.

The value obtained in blank assay ΔT_s was found by measuring on a solution without the estimated amine under equal reaction conditions.

It is obvious from Table 1 that the value found in blank assay as well as the relative error suddenly drops if the concentration of hydrochloric acid attains the value of 0.15 M-HCl.

Table 1

Dependence of the error of measurement and of the value of blank test on the concentration of hydrochloric acid for the determination of sulfanilic acid with a 0.5 M solution of sodium nitrite

Concentration of HCl mol dm ⁻³	0.05	0.1	0.15	0.2	0.25	0.5	1.0
ΔT_s mm	29	17	9	6	6	5.5	3
ϵ_r %	2.38	1.58	0.71	0.75	0.72	0.67	0.74

The effect of the heat of reaction (C) is in a considerable degree reduced by the use of the method of double injection (similarly as the effect of the heats of dilution), which is explained in the subsequent exposition. At the first injection of reagent, the reaction heat of this preceding reaction is produced simultaneously with the reaction heat of the investigated reaction itself, *i.e.* diazotization or nitrosation and the resulting temperature change $\Delta T'$ is equal to

$$\Delta T' = -c_A v_A \frac{\Delta H_r}{C} - c_B v_B \frac{\Delta H_{r,c}}{C} \quad (1)$$

where c_B , v_B , $\Delta H_{r,c}$, ΔH_r , C , c_A , and v_A are the concentration of active component of reagent, volume of reagent, molar enthalpy change of reaction (C), molar enthalpy change of reaction (A) or (B), overall heat capacity of system after the first injection of reagent, concentration of sample, and volume of sample. For simplicity, the heats of dilution have been omitted and equal temperatures of the sample and reagent in the interval before injection and full extent of all reactions are assumed.

On equal suppositions, the temperature jump at the second injection may be expressed by the following equation

$$\Delta T'' = -c_B v_B \frac{\Delta H_{r,c}}{C + C_B} \quad (2)$$

where C_B is the increment of heat capacity due to the injection of reagent.

As the enthalpograms are evaluated from the difference $\Delta T = \Delta T' - \Delta T''$ (Fig. 1), the heat of auxiliary reaction (C) appears only as the term $-c_B \Delta H_{r,c} \cdot \nu_B C_B / C(C + C_B)$. Of course, that holds on condition that reaction (C) can proceed quantitatively at the second injection of reagent, too. Therefore, free hydrochloric acid has to be still present in the reaction mixture.

The number of mmoles of hydrochloric acid in the analyzed solution of amine should be, therefore, greater than the number of mmoles of sodium nitrite in both doses of reagent, which corresponds to 20 cm³ of 0.175 M-HCl for 2×1.5 cm³ of 1 M-NaNO₂. Then reaction (C) proceeds to full extent even at the second injection and the investigated value of ΔT is practically affected solely by the concentration of sample c_A .

As obvious from Table 1, this result was confirmed experimentally. By comparing all results, we can deduce that the optimum concentration of hydrochloric acid is 0.5–1.0 M. The possibility of determining amines in the presence of more concentrated hydrochloric acid (2.5–5.0 M) was also investigated. However, in this case, a considerable heat of dilution is released, which results in the increase in the error of measurement.

For the amines which are poorly soluble in water, a convenient solvent must be used. Usually a mixture methanol–water in a proportion which enables us to maintain the dissolved amine in necessary concentration (at least 5×10^{-2} M) and at the same time at least the 1 M concentration of sodium nitrite is suited. Another problem consists in the fact that the reaction rate decreases with increasing proportion of nonaqueous solvent.

By respecting all these conditions, it has been ascertained that a mixture methanol–water in the ratio 1:1–5:1 should be used to fulfil all the above stipulations concerning the course of reaction.

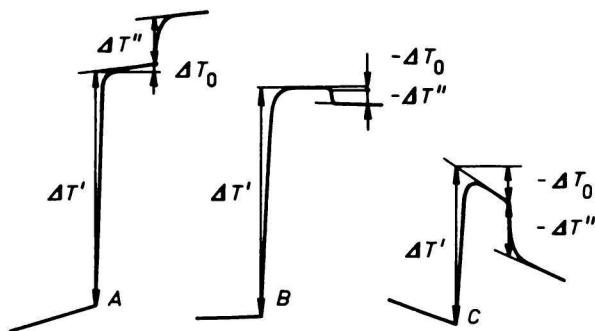


Fig. 1. Evaluation of the enthalpograms obtained by the method of double injection.

A — Temperature of reagent higher than the temperature of sample $\Delta T_{BA} > 0$; B — $\Delta T_{BA} \approx 0$;
C — $\Delta T_{BA} < 0$.

The upper limit of determination of the investigated amines is governed by their solubility in a given solvent (water, methanol). This solubility varies about the value 5×10^{-2} M for most amines. If it is higher (aniline), the upper limit is restricted by the amount and concentration of reagent. If we use a solution of nitrite of about 1 M concentration, then the maximum determinable concentration of amine (if we pipette 20 cm³ of solution) varies about the 5×10^{-2} M value. In this case, a sufficient excess of reagent is still secured and the merit of the method is preserved (a shift of reaction equilibrium to the right side), which facilitates a rapid course of reaction. It would be possible to use a more concentrated reagent and thus to shift the upper limit of determination to 5×10^{-1} M solutions of amines. However, the value obtained in blank assay and the lower limit of determination would be raised in this way, too.

As ensues from experimental data, the lower limit of concentration of the investigated solutions may be considered to be represented by about 1×10^{-3} M solutions of amines. The lower concentrations of amines were also investigated. But the calibration graph considerably bends in these cases and the error of determination reaches 10% (rel.) and more.

Nevertheless, these conclusions refer to the conditions of measurements. It is not beyond all questions whether the concentrations under 10^{-3} M could be determined in other cases, e.g. at a lower concentration of reagent and the use of temperature-controlled solutions. The 10^{-3} — 5×10^{-2} M solutions of samples may be regarded as the optimum concentration range of amines in our case.

The influence of potassium bromide on the rate of diazotization was studied in systems where aniline was determined in the presence of nitrobenzene. Owing to the insolubility of nitrobenzene in water, the mixed medium methanol—water had to be used. Because of the presence of methanol, the diazotization rate of aniline decreases so much that the reaction is not useable for enthalpimetric determination (irrespective of the method used). By the addition of potassium bromide, it is, however, so accelerated that it may be used for analytical determination. It has been established that the optimum concentration of bromide is dependent on the concentration of chloride ions, i.e. mainly on the concentration of hydrochloric acid. For 2 M-HCl, the most convenient concentration of bromide is 4×10^{-2} M.

In the use of the method of double injection of reagent [14], it is also necessary to appraise the maximum difference between the temperature of reagent T_B and the temperature of the reaction mixture containing the sample T_A before the first injection, $\Delta T_{BA} = T_B - T_A$, or the temperature change of the reaction mixture between both injections, ΔT_0 (Fig. 1), while the fixed maximum still admissible relative error of determination is to be respected. An approximate procedure has been given in [14] and a more detailed description is to be found in [15, 17]. The estimates of boundary conditions for 2% admissible error, different volumes of

reagent, 20 cm³ of reaction mixture, and the thermal capacity of Dewar vessel of 42 J K⁻¹ are given in Table 2.

Table 2

Allowed values of the initial temperature difference between reagent and sample (ΔT_{BA}) and the temperature drift between both injections (ΔT_0 , °C) at the maximum 2% error of determination

Determined substance	0.002 M ΔT_{BA}	0.5 cm ³ ΔT_0	0.01 M ΔT_{BA}	1 cm ³ ΔT_0	0.05 M ΔT_{BA}	1.5 cm ³ ΔT_0
<i>p</i> -Aminobenzoic acid	1.2	0.036	1.4	0.1	3	0.3
Sulfanilic acid	2.4	0.08	3	0.2	6.5	0.65
<i>o</i> -Toluidine	2	0.06	2.3	0.15	5	0.5
Aniline	1.3	0.04	1.6	0.1	3.6	0.36
α -Naphthylamine	1.4	0.045	1.7	0.1	4	0.4
Benzidine	2.4	0.07	3	0.2	6.5	0.65
Diphenylamine	0.65	0.02	0.8	0.05	1.8	0.2

Data in the heading of the table give the concentration of the amine determined and the amount of injected reagent. The volume of solution is 20 cm³ and the heat capacity of vessel 42 J K⁻¹.

The allowed temperature intervals are directly proportional to the concentration of the amine determined, the values of reaction heats, and the admissible maximum error but approximately inversely proportional to v_B^2 (in case of ΔT_{BA}) or v_B (in case of ΔT_0). Therefore, it is convenient to use the optimum volume of injected reagent v_B with respect to sufficient excess of reagent and sufficiently large allowed temperature interval ΔT_{BA} and ΔT_0 .

For larger series of determinations, the modified coefficient method [15] may be applied. This method enables us to use the solutions which are not at all temperature-controlled.

Experimental

Chemicals and apparatus

All chemicals used were anal. grade reagents. The solutions of aromatic amines of 0.05 M concentration and higher were prepared by weighing the requisite amount of sulfanilic acid, *p*-aminobenzoic acid, aniline, *o*-toluidine, α -naphthylamine, benzidine, and diphenylamine (Lachema, Brno). The 0.5 and 1.0 M solutions of the injected reagent (sodium nitrite) were prepared from the preparation of Merck (Darmstadt).

A thermometric equipment described earlier [14, 16] was used for measurements. This equipment consists of a Dewar vessel in which a stirrer driven by electric motor is placed.

The inlet of the injecting pipette through which the reagent sucked from the stock flask is injected leads into that vessel. The measured thermal effect is taken by means of a thermistor serving as a thermosensor. The thermistor is connected in one of the arms of a Wheatstone bridge which is fed by a flat 4.5 V battery through potentiometers used as voltage dividers. The thermistor is linearized by means of a resistor connected in parallel. The outlet of the bridge is connected to a compensation recorder EZ 2 (Laboratory Instruments, Prague).

More detailed data and theoretical analysis of the method have been given earlier [14—19] and are discussed in [20].

Working procedure for the determination of aromatic amines

The weight amount is always so chosen according to the assumed content of amines that the total concentration of solution varies about the 10^{-2} M value. 0.2—1.0 M concentration of hydrochloric acid may be regarded as the most convenient for the determination of amines.

The searched values of concentrations are read on a calibration graph which has been constructed as follows. The aqueous 2.5×10^{-3} — 3.75×10^{-2} M calibration solutions of amines and the solution for blank test are prepared. All solutions also contain hydrochloric acid in about 0.5 M concentration. The injected reagent is the 1 M aqueous solution of sodium nitrite.

The calibration graph for α -naphthylamine, diphenyl, and benzidine may be constructed analogously, the only difference being that the measurements should be performed in the mixed medium methanol—water (3:1). A set of 2.5×10^{-3} — 3.75×10^{-2} M solutions (in case of benzidine 2×10^{-3} — 3×10^{-2} M solutions) and a solution for blank test are to be prepared. The content of hydrochloric acid is equal as in the preceding case. The injected reagent is 1 M- NaNO_2 in the mixed solvent methanol—water (3:1).

First of all, it must be checked whether the temperature of reagent and the surrounding temperature are equal. The temperature of sample is so adjusted that it does not differ from the surrounding temperature more than by ΔT_{BA} the value of which is given in Table 2. 20 cm^3 of solution are always pipetted into the Dewar vessel and a convenient bridge voltage is set. After switching on the stirrer, the temperature trend is recorded and the first injection ($\Delta T'$) of reagent (usually 1—1.5 cm^3) carried out. Immediately after recording, the second injection of equal amount of reagent is carried out which manifests itself by the temperature change $\Delta T''$. Thus the calibration graph represents the relationship $\Delta T = f(c)$ while it holds $\Delta T = \Delta T' - \Delta T''$. In evaluating the temperature jumps, the trends are extrapolated to the moment of injections (Fig. 1).

Determination of aniline, o-toluidine, p-toluidine, p-aminobenzoic acid, and sulfanilic acid

The sample of amine (1.0 g) is put into a 100 cm^3 graduated flask, dissolved in distilled water, acidified with concentrated hydrochloric acid (5 cm^3), and filled up to the mark with water. This solution (20 cm^3) is pipetted and transferred into the Dewar vessel. Further

procedure and measurements are carried out in usual way. The reaction agent is a 1 M aqueous solution of sodium nitrite. The concentration of amine is read on the calibration graph.

Determination of α -naphthylamine, diphenylamine, and benzidine

The sample (1.5 g, in case of benzidine 1.0 g) is put into a 100 cm³ graduated flask, dissolved in methanol (anal. grade) (75 cm³), acidified with concentrated hydrochloric acid (5 cm³) and filled up to the mark with distilled water. Further procedure is equal as described earlier. In this case a 1 M solution of sodium nitrite in the mixed medium methanol—water (3:1) is used as reaction agent.

Determination of aniline in the presence of nitrobenzene

Aniline may be successfully determined even in the presence of nitrobenzene because nitrobenzene does not react with nitrous acid under the conditions used for the determination. Because of the insolubility of nitrobenzene, the mixture methanol—water (3:2) has to be employed. However, the rate of diazotization must be raised by adding potassium bromide in 4×10^{-2} M concentration (450 mg in 100 cm³ of solution). The determination is performed in the medium of 2 M-HCl.

Working procedure

The weighed sample (10.0 g) of an aniline—nitrobenzene mixture is dissolved in methanol (anal. grade) (100 cm³). 25 cm³ of this solution are pipetted and transferred into a 250 cm³ graduated flask. Afterwards, 50 cm³ of concentrated hydrochloric acid, 20 cm³ of 1 M-KBr, and 125 cm³ of methanol are added. On cooling, the flask is filled up to the mark with distilled water. 20 cm³ of this solution are pipetted and transferred into the reaction vessel of the equipment. Further procedure and measurements have been already described.

Conclusion

It has been revealed that the diazotization and nitrosation reactions may be used for a direct enthalpimetric determination of primary and secondary aromatic amines. It appears that the procedure with double injection of reagent is especially suited for this purpose because of the simplicity of instrumental equipment and easy manipulation.

By investigating the optimum reaction conditions, it has been found that the most accurate results are to be achieved if the concentration of hydrochloric acid varies in the range 0.2—1.0 M. The same is valid for α -naphthylamine, diphenylamine, and benzidine. But in this case, the mixed methanol—water medium should be used because of low solubility of the substances to be determined. The ratio of components in the mixture may vary from 1:1 to 5:1, the

optimum being 3:2. For these amines, no addition of potassium bromide is necessary even in this mixed medium. The reaction proceeds rapidly enough in spite of the negative influence of methanol.

On the other hand, methanol so retards the course of diazotization of aniline that the reaction is not useable for the enthalpimetric method proposed. Therefore, it is necessary to add potassium bromide which accelerates the reaction sufficiently. The optimum concentration of bromide depends on the concentration of chloride ions, *i.e.* mainly on the concentration of hydrochloric acid. For 2 M-HCl, the most convenient concentration of bromide is 4×10^{-2} mol dm⁻³.

Therefore, we may assume that the 5×10^{-3} – 5×10^{-2} molar solutions correspond to the optimum concentration range for the determination. We can successfully use even 10^{-3} molar solutions for the determination but the relative error thereby reaches the value of ± 5 – 10% .

All determinations have been subjected to statistical evaluation from which it follows that the method gives results that are accurate enough. The error of determination evaluated according to Student's test for the probability of 0.95 amounts to $\pm 0.78\%$ (rel.). For the determination of aniline in the presence of nitrobenzene, the value of $\pm 0.77\%$ (rel.) has been found.

Besides amines, the method was checked by the use of other substances which underwent nitrosation. For instance, resorcinol may be very well determined with the relative error of $\pm 0.50\%$.

All experimental results demonstrate that the suggested enthalpimetric method can be compared with many other methods for the determination of amines, *e.g.* potentiometric and photometric methods, thermometric titrations, *etc.* In contrast to other methods of injection enthalpimetry, the method of double injection does not necessitate any temperature control by means of a thermostat. An approximate temperature adaptation is sufficient. Therefore, the suggested method can be recommended for a rapid determination of primary and secondary aromatic amines and, if need be, other substances which analogously react with nitrous acid.

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