

THE INFLUENCE OF SOME ELEMENTS ON MICRODETERMINATION OF NITROGEN IN ORGANIC SUBSTANCES BY DIGESTION WITH SULPHURIC ACID IN SEALED TUBE

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A procedure for determination of nitrogen in organic substances containing N—H, N—C, and N—Me bonds by digestion with sulphuric acid in sealed tube and subsequent oxidimetric titration of formed ammonium salts is reported. The effects of some elements (halogens, Fe, Cu, Ni, Co, Hg, Pd, Pt, and Rh) on both mineralisation and titration course were examined and optimum conditions were established.

Determination of nitrogen in organic substances after digestion with sulphuric acid in sealed tubes has several advantages, compared to the Kjeldahl method. The digestion can be carried out at an elevated and easily controlled temperature, and the dangers of contamination of the mineralisation mixture by ammonia from surrounding air and of the losses, either mechanical or due to the volatility of ammonium sulphate, are avoided. The digestion in a sealed tube, suggested first for the sample size of several hundreds of milligrams, proved especially advantageous for milligram to microgram samples. In connection with decreasing sample size, the classical evaluations of the ammonia content in digestion mixture by the steam distillation followed by acid-base titration or by photometry was replaced by oxidimetric titration with a hypochlorite solution in the presence of bromide ions. The visual indication of this titration used by Kolthoff and Stenger¹ was due to Tomíček and Filipovič² later replaced by potentiometric indication, and finally by biamperometric indication due to Řezáč and Figarová³. For determining nitrogen in microgram samples Belcher and coworkers⁴⁻⁶ used this titration with iodometric visual end point estimation. Digestion of organic nitrogen-containing substances by sulphuric acid in sealed tube, followed by direct oxidimetric titration of the ammonia formed, is particularly suitable for determination of nitrogen in organometallic compounds, in contradistinction to various modifications of the Dumas method which in this case frequently fail⁷. Despite of this fact, optimum conditions for digestion of organometallic compounds, *i.e.* the composition of digestion mixture, temperature, and time, have not yet been established.

In connection with the analysis of complex catalysts we examined in the present work the digestion conditions for nitrogenous compounds containing Fe, Ni, Co, Cu, Pt, Pd, Rh, and halogens, and studied the effect of these components on the course of subsequent oxidimetric titration of ammonium ions. We limited ourselves to the compounds with N—C, N—H, and N-metal bonds which did not contain N—O or N—N bonds.

EXPERIMENTAL

Reagents and apparatus. Sulphuric acid, *p.a.* (Lachema, Brno) was purified by vacuum distillation. KBr and KHCO_3 were samples of *p.a.* purity grade (Merck, Lachema), 0.01M sodium hypochlorite solution was prepared by diluting a technical concentrated solution (Spolana, Neratovice) and was stored in a dark flask. The value of this solution was determined by titration of the known amount of ammonium sulphate standard solution and was checked before commencing each series of analyses. Distilled water was freed of trace amounts of ammonia by redistillation in a glass apparatus which was carried out with the addition of sulphuric acid and potassium permanganate. The purity of standard compounds was checked by elemental analysis or by melting point determination. Test tubes from the borosilicate glass (7.5 mm i.d., 1 mm thick, 11 cm long) were cleaned prior to using by chromosulphuric acid, then rinsed with water and dried. Digestion was carried out in a vertical oven equipped with temperature control up to 600°C. Biamperometric titrations were performed with the pair of platinum plate electrodes (approx. 0.5×0.5 cm) with 250 mV applied voltage. The values of the current during reaction were read on a Galvanometer DG-20 (Metra, Blansko).

Procedure. A 2–7 mg sample was weighed to a clean test tube, then 0.5 ml of concentrated sulphuric acid was added, and the tube was sealed 2–3 cm below the open end. The tubes were placed into the oven and heated at 420°C for 1 h. After completion of digestion, the cool tubes were rinsed with water and dried. Before their opening, the ampoules were cooled with a dry ice–ethanol mixture to –50 to –60°C to lower the pressure of sulphur dioxide. The content of the tubes was transferred to 100 ml-beakers and boiled for 5 min, to expell sulphur dioxide. After cooling the solution, 1 g of potassium bromide was added, and traces of reducing compounds eventually present were titrated with the hypochlorite solution, using biamperometric indication. Titration curve was of V-shape with slowly descending initial part of the curve, which, after having reached the end point, steeply rises. This consumption equaled usually to 2–3 drops, provided that sulphur dioxide was well boiled off. The pH value of the solution was adjusted to approx. 8.0–8.5 by adding portionwise a total of 6 g of potassium hydrogen carbonate. The solution was again titrated biamperometrically with sodium hypochlorite. The titration curve was of the reversed L-shape. The end point was determined graphically. With each series, two blank experiments were run in the same way.

In determining nitrogen in substances containing also some metal ions the digestion procedure and titration had to be somewhat modified, as will be described later.

RESULTS AND DISCUSSION

Digestion conditions were studied by several authors. The temperature 470°C for 15 min suggested by White and Long⁸, was found too high, since the results obtained were low^{9,10}, and a 420–430°C temperature range has been recommended as an optimum region. In several cases digestion was carried out at 380°C (ref.⁶) or even at 350°C (ref.⁵), if nitrogen had to be determined in the presence of other elements. Kirk and coworkers¹⁰ have proved that the losses of ammonia by digestion at high temperatures are not due to the decomposition $2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$, but that at temperatures around 500°C the ammonia is oxidised to nitrogen and SO_3 is reduced to SO_2 , which reactions are accompanied by formation of water. The authors also found that a small amount of water added to the reaction mixture markedly suppresses

the oxidation of ammonia. In this work we examined the effect of temperature over a 340–460°C region in digestion of 1,10-phenanthroline⁸ under conditions described in Experimental part. Following results were obtained (these are expressed in per cent of theoretical content of nitrogen):

Temperature, °C	340	380	420	460
Found N, %	88.1–93.3	99.1–100.2	100–100.1	91.0–94.7

Concerning the time of digestion, 0.5–2 h have been recommended. In our experiments the values of nitrogen content in standard compounds obtained in experiments which were carried out at optimum temperature over a period of 30–120 min deviated within experimental errors. According to our experience, digestion at optimum temperature conditions is complete even in the absence of catalyst, although the addition of a mercuric salt was recommended.

The precision and accuracy of the procedure as a whole were verified by analyses of standard compounds containing N–C and N–H bonds. The results obtained are presented in Table I. The standard deviation, calculated from the results of all experiments ($n = 30$), equaled to 0.082%. In these analyses two parallel determinations were always carried out. For each series of analyses a blank experiment was run twice. In this experiment the consumption of volumetric solution depended on the purity of the chemicals used. In our experiments it corresponded to a value of approx. 0.006 mg N. The nitrogen content in analysed sample should not be lower than 0.4%.

The interfering effect of other elements on this determination has thus far attracted little attention. Belcher and coworkers found that the sulphur bonded in organic compounds is converted to sulphur dioxide and chlorine to hydrogen chloride, so that both elements do not interfere with the determination. Iodine is converted to both hydrogen iodide and elemental iodine; both forms can be titrated with the hypochlorite.

TABLE I

Results of Nitrogen Determination in Standard Compounds

Sample size 2–7 mg, \bar{x} the mean value, s the standard deviation, n the number of analyses.

Standard	Calculated, %	\bar{x} , %	s	n
Acetanilide C_8H_9NO	10.36	10.35	0.088	9
1,10-Phenanthroline $C_{12}H_8N_2$	15.55	15.56	0.071	12
Terephthalodinitrile $C_8H_4N_2$	21.86	21.86	0.087	10

At 350°C and with mercuric sulphate as a catalyst, only iodine is formed and can be removed by boiling. Interfering bromine can be removed similarly. In analyses of nitrogenous substances containing platinum or transition metals and halogens, following interfering effects could occur: stable ammine complexes are formed which release ammonia at a slower rate during the titration; the element which is the central atom is transformed during digestion to such a form which under given conditions is also titrated by the hypochlorite; this element catalyses the oxidation of ammonia to nitrogen under digestion conditions. As we have found, cobalt, nickel, copper, and mercury do not exhibit interfering effect. These metals were added as sulphates to the weighed samples of acetanilide and phenanthroline. The experimental nitrogen content agreed well with calculated values.

Iron is present in the reaction mixture after digestion as Fe(III) and Fe(II). The oxidation of Fe(II) by hypochlorite solution in acidic medium together with decomposition of the residual sulphur dioxide could not be used, since it proceeded at a very slow rate, even in the presence of chloride or fluoride ions which were added to increase the values of the redox potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system. The complete oxidation of Fe(II) can be readily achieved by passing for about 10 min oxygen through the solution after its neutralisation with sodium hydrogen carbonate. The precipitate of iron salts does not interfere with the titration. Iodine and iodide are oxidised by the hypochlorite in both acid and hydrogen carbonate media to higher oxidation states. Therefore iodide is converted first to iodine by adding a small amount of iron(III) salt in an acidic medium, and then iodine is removed by a 15 min-boiling. The Fe(II) formed is then converted to Fe(III) by the above mentioned procedure. Bromine remains in the solution after digestion as bromide or as free bromine, which is removed analogously as iodine.

For the investigation of the effect of platinum, palladium, and rhodium, each of these metals (always 1 mg) was added to the weighed samples of acetanilide or phenanthroline in the form of chlorides or potassium salts of chloro complexes, and these mixtures were analysed by standard procedure. The results did not show any systematic error. After completion of digestion, palladium appears in the form as a brown-red precipitate which dissolves after diluting the mixture with water. We observed that during titration the oxidation of ammonia proceeds at a slower rate, which is believed to be due to the presence of stable palladium–ammine complexes. This is the reason why the current increases already before the end point and only slowly decreases to the original value, so that titration must be carried out carefully. The end point can be however determined with sufficient accuracy. Titration of the standard solution of ammonium salt in the presence of palladium ions proceeds analogously.

Platinum(IV) and rhodium(III), when added to the standard solution of ammonium salt, do not affect the course of the hypochlorite titration of ammonia. The titration follows expected course, even in the event that ammonium salt was heated first

in an open beaker with sulphuric acid in the presence of Rh or Pt. After completion of digestion in a sealed tube, platinum appeared in the form of a grey spongy material, and rhodium in the form of a red precipitate. After dilution with water and boiling, both precipitates dissolved and subsequent titration followed expected course. However, the results found were substantially lower than calculated values. More satisfactory results cannot be achieved even by reducing both metals with aluminium in an acidic medium. It seems likely that under digestion conditions platinum and rhodium catalyse the oxidation of ammonium ions to nitrogen. The interfering effect of these metals has been eliminated by decreasing the digestion temperature to 380°C and by diluting the sulphuric acid with water (0.1 ml of water per 0.5 ml of concentrated sulphuric acid). Under these conditions the analyses followed ex-

TABLE II

Effects of Temperature and Sulphuric Acid Concentration on Determination of Nitrogen in the Presence of Pd, Pt, and Rh

Standard compounds: A acetanilide, B 1,10-phenanthroline (2—7 mg).

Standard	Added 1 mg	Temperature °C	H ₂ SO ₄ concentration, %	Found % N	Deviation rel. %
A	Pd	420	98	10.33	- 0.3
				10.42	+ 0.6
B	Pd	420	98	15.50	- 0.3
				15.67	+ 0.8
A	Pt	420	98	9.77	- 5.7
A	Pt	380	98	8.45	-18.4
				10.09	- 2.6
A	Pt	420	80	10.01	- 3.4
				10.16	- 3.0
A	Pt	380	80	9.86	- 4.8
				10.36	0.0
B	Pt	380	80	10.40	+ 0.4
				15.52	- 0.2
A	Rh	420	98	15.49	- 0.4
				6.15	-40.6
A	Rh	380	98	7.13	-31.2
				9.98	- 3.7
A	Rh	420	80	9.15	-11.7
				9.22	-11.0
A	Rh	380	80	8.83	-14.8
				10.28	- 0.8
B	Rh	380	80	10.38	+ 0.2
				15.60	+ 0.3
				15.50	- 0.3

pected course and the errors of the results did not exceed experimental errors (Table II).

The method is particularly suitable for analyses of substances containing nitrile groups, which compounds could release volatile hydrogen cyanide during digestion in an open vessel. The method was used to analyse a variety of homogeneous or polymer-supported catalysts which comprised coordination compounds of platinum, palladium or rhodium halides with the nitrile, secondary or tertiary amine groups attached to a poly(styrene-divinylbenzene) skeleton. As these substances were not defined compounds, the accuracy of the method could not be estimated. Its precision was evaluated by comparing the results of repeated analyses. At the nitrogen content from 0.4 to 4.0%, deviations from the mean value of two or three analyses did not exceed $\pm 0.05\%$.

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