Accuracy in Gravimetric Determination of Nitrate and Nitrite as Nitron Nitrate

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The accuracy of nitron-method gravimetry for the determination of the purity of potassium nitrate and that of sodium nitrite was studied. The gravimetry of potassium nitrate was compared with that of nitric acid determined by an acidimetric coulometric titration. The concentration of nitrate ions left in the filtrate of the nitron nitrate precipitate was measured by ion chromatography. A method for the oxidation of nitrite ions to nitrate ions by permanganate ions was studied for the purpose of the application of the nitron-method to the determination of the purity of sodium nitrite. The small quantity of nitrate ions contained in sodium nitrite was determined by ion chromatography.

With the recent developments of instrumental analysis methods such as ion chromatography, reference solutions of various anions and cations have been used for the instrument calibration. A reference solution of nitrate ion or of nitrite ion is most popular. To assure the reliability of such solutions as certified reference materials, the concentration of each solution or the purity of a raw material for the solution has to be determined by some absolute or definitive method that provides property values traceable to fundamental units of measurement:[1] e.g., gravimetry or coulometric titration based on Faraday's law. Though there are several reports on the coulometric titration of nitrate or nitrite ion[2-4] on the basis of a chemical reaction, the precision and accuracy achieved there are not so satisfactory. It is known that nitrate ion reacts with nitron (1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole)[5-10] (Fig. 1) to form an insoluble salt.[11,12] Though this reaction has been utilized to determine nitrate ions[13-16], the accuracy of the method has not been considered sufficiently.
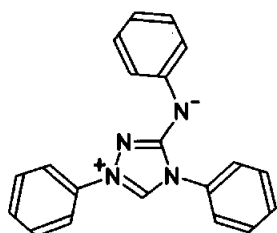

Fig. 1   A resonance structure of nitron as a meso-ionic compound.

In the present study, the accuracy of the nitron method for nitrate ions has been examined with a nitric acid solution which was analyzed by an acidimetric coulometric titration.[17,18] The quantity of nitrate ions left in the filtrate was checked by ion chromatography. The nitron method was also applied to the determination of nitrite ions by oxidizing nitrite to nitrate prior to the gravimetry. Since the reagent sodium nitrite used contained a small amount of nitrate, an attempt was also made to determine the nitrate in nitrite by ion chromatography.

Experimental

Reagents

Reagent-grade chemicals were used unless otherwise stated. Ultrapure nitric acid and sulfuric acid were available from Kanto Chemical Co., Tokyo. According to the manufacturer, concentrations of chloride ions, sulfate ions and phosphate ions in the nitric acid were less than 1×10^{-5} wt%. Water was purified by sub-boiling distillation of deionized water. On the basis of a preliminary check, potassium nitrate and sodium nitrite were dried at 130°C for 4 h and at 110°C for 4 h, respectively. A potassium nitrate solution and a sodium nitrite one were prepared by dissolving ca. 8.06 g of the dried potassium nitrate and ca. 8.15 g of the dried sodium nitrite, respectively, in 1 kg of water. Each sample solution was kept in a Teflon-PFA bottle. Correction for buoyancy was always considered. Ten wt% nitron solution was prepared by filtering without suction of a mixed solution of both 85 cm³ of water and

5 cm^3 of acetic acid, containing 10 g of nitron, with a glass filter of medium porosity (G3 grade); the resulting clear solution was protected from light. A potassium permanganate solution (0.02 mol dm^{-3}) was prepared according to the literature[19], except for the gentle boiling for 90 min and the filtration by means of suction with a glass filter of fine porosity (G4 grade). The chemical formula weights used for KNO$_3$, NaNO$_2$ and nitron nitrate (C$_{20}$H$_{16}$N$_4$·HNO$_3$) are 101.10, 69.00 and 375.39, respectively.[20]

Apparatus

An IC500P ion chromatographic analyzer (Yokogawa Electric Co., Tokyo) was used for the determination of nitrate ions in the reagent sodium nitrite and in the filtrate of the nitron precipitate. The analyzer was equipped with a separator column (model SAX1-205, together with a PAX1-035 precolumn) and a suppressor (model CX1). Weighing was carried out on a Mettler balance (0.1 mg sensitivity). The density of each solution was determined with a DA-101B automatic densimeter (Kyoto Electronics, Kyoto).

The constant-current source used for coulometric titration is a model 220 type (Keithley Instruments, Cleveland). The accuracy of the electrolysis currents was checked by using Type-2792 standard resistors (10 Ω and 100 Ω, Yokogawa), a digital voltmeter (Model 8800A, John Fluke Mfg. Co., Seattle) and a Type-2749 unsaturated Weston standard cell (Yokogawa). The coulometric-titration cell used is schematically shown in Fig. 2, which is a little different from the original design of Taylor and Smith.[17] This is made of Pyrex glass and equipped with silicon rubber stoppers.
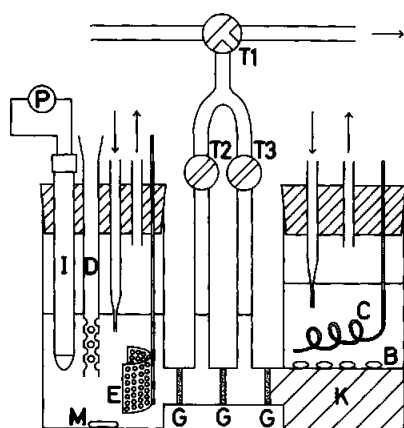

Fig. 2 Electrolysis cell for hydroxide-ion generation. B: barium carbonate powder; C: counter electrode (a platinum wire of 1.5 mm radius and *ca.* 150 mm long); D: sample-inlet tube; E: platinum generating electrode whose surface area is 10 cm^2 (one side); G: sintered glass disks (G3, G3 and G4 grade from the left hand); I: combination glass electrode; K: agar gel (100 cm^3 of 3% agar in 1 mol dm^{-3} potassium chloride); M: stirring bar; P: pH meter; T1, T2, T3: stop cocks. The arrows show the flow of nitrogen gas.

The generator-electrode chamber where a titrant is electrogenerated is connected to a bubble trap to exclude air. The sample-inlet tube, part of which is immersed into an electrolytic solution and perforated, was sealed with PARAFILM except when a sample solution was introduced. The tube enabled us to introduce a sample solution without removing the silicon rubber stopper. The temperature of solutions was 23±0.5°C. The electrolytic solution volumes in the cathode chamber and in the counter–electrode chamber were 100 cm^3 and 90 cm^3, respectively, of 1 mol dm^{-3} potassium chloride solution. Barium carbonate powder was placed in the counter-electrode chamber to neutralize the acid generated.[21] For an end-point detection, a D-150A pH-meter (TOA Electronics, Tokyo) was used with a pH combination electrode (GST-5211C, TOA).

Density of nitron nitrate crystal

The density D of nitron nitrate crystal was measured at 25°C with a Hubbard type pycnometer. Since the crystal hardly dissolves into water, D can be calculated with the following equation:[22]

$$D = \frac{(b-a)S-(c-d)/(1/\rho+1/w)}{(b-a)-(c-d)} \tag{1}$$

where a is the weight of the pycnometer alone, b is the weight of it containing the nitron nitrate crystal, c and d are the weights of the pycnometer filled with water in the presence and absence, respectively, of the nitron nitrate crystal, S and ρ are the densities of water and air, respectively, and w is the density of a weight for calibration of the balance used. a, b, c and d are the values before the correction for buoyancy. The D value obtained was 1.37±0.01 g cm^{-3}.

Procedure

Gravimetry of nitrate. A 20-g portion of *ca.* 8.06 g kg^{-1} potassium nitrate solution was weighed into a 300-cm^3 beaker. Fifty cubic centimeters of water and 1 cm^3 of 0.5 mol dm^{-3} sulfuric acid solution were added. The solution was heated almost to boiling and then 10 cm^3 of 10 wt% nitron solution was added. After being cooled a little, the solution was kept at *ca.* 5°C for *ca.* 20 h. The needle-like crystal which formed was filtered by means of suction with a glass-filter crucible (1G4 grade). The beaker was rinsed with the filtrate, which was added into the crucible; this procedure was repeated again. The crystal in the crucible was washed with 10 cm^3 of the nitron-nitrate-saturated aqueous solution which had been kept at *ca.* 5°C, was dried at 110°C for 2.5 h; then it was cooled in a silica-gel desiccator and was weighed. Blank tests were carried out simultaneously. For a nitric acid solution, a potassium hydroxide solution required to neutralize the acid was added after sampling, followed by the same procedure as for the potassium nitrate solution.

Gravimetry of nitrite. A 36-cm^3 portion of 0.02 mol kg^{-1} potassium permanganate solution and 1 cm^3 of

concentrated sulfuric acid were put in a 300-cm³ beaker. Into the solution, while it being stirred with a magnetic stirring bar, a 15-cm³ portion of *ca.* 8.15 g kg⁻¹ sodium nitrite solution was slowly added under the surface of the solution with a calibrated transfer pipet; the temperature of the sodium nitrite solution was *ca.* 25°C. A different pipet was used for each addition of the sodium nitrite solution. Then 0.05 mol dm⁻³ sodium oxalate solution was added to reduce the excess permanganate ion until the pink color vanished. The solution was warmed a little; 0.02 mol dm⁻³ potassium permanganate solution was dropwise added until the pink color just remained. After an immediate addition of 1 cm³ of 2.0 mol dm⁻³ formic acid, the solution was kept at the laboratory temperature for *ca.* 30 min. The magnetic stirring bar was then removed carefully with a magnet. The volume was adjusted to *ca.* 100 cm³ with water. The same procedure as that for nitrate ion was then followed, starting with the heating almost to boiling. The potassium nitrate solution was also analyzed in parallel by the same gravimetric method with potassium permanganate, except that a 22-g portion of the sample solution was weighed into a 300-cm³ beaker before the addition of a 36-cm³ portion of 0.02 mol dm⁻³ potassium permanganate solution. Blank tests were also carried out in parallel.

Coulometric titration of nitric acid. The point corresponding to pH 7 was adopted as an end point, which was very close to the inflexion point, *i.e.* the equivalence point in this case. The value for the Faraday constant used is 96485 C mol⁻¹.[23–25] Pure nitrogen gas was always admitted into the electrolytic solution in the counter-electrode chamber. After nitrogen gas was admitted for 1 h to remove the carbon dioxide dissolved into the generated medium (pH 5.2), electrolysis was carried out with a 1-s pulse of 10 mA up to a pH value of *ca.* 8, when *ca.* 80% capacity of the center compartments was occupied by the electrolytic solution. It took 2 min to reach a stable value of pH. The solution in the center compartments was moved into the cathode chamber with the nitrogen-gas pressure according to the literature.[17] After the procedure was repeated several times until the solution was perfectly mixed, the pH value was recorded and used to estimate a first end point from the titration curve. The gas-inlet tube in the cathode chamber was partially pulled up to let nitrogen gas flow over the surface of the generated medium. Nitrogen gas was always admitted into the solution or above it. A 5-g portion of a sample solution was introduced into the cathode chamber with a gravimetric buret through the sample-inlet tube, which was immediately rinsed with 5 cm³ of water. The generated medium was electrolyzed with a continuous current of 50 mA until the indicator electrode indicated a pH value of *ca.* 5.4, when the electrolysis had proceeded to *ca.* 99.7% of the completion. After nitrogen gas was admitted again into the solution for 1 h to exclude the carbon dioxide introduced by sampling, the gas-inlet tube in the cathode chamber was partially pulled up

above the surface of the solution. An end point was found by the electrolysis with a 1-s pulse of 10 mA in the same way as done for the first end point. Since the relative efficiency of the pulse current to the continuous current was 99.7%, the error resulting from the pulse current could be neglected. Three successive measurements with each 5-g portion of a sample solution were carried out in the same generated medium.

Ion chromatography. The signals of ion chromatography were detected with a conductometric or an absorptiometric method. The separator column was kept at 40°C or 45°C. The eluent used contained 4×10⁻³ mol dm⁻³ sodium carbonate and 4×10⁻³ mol dm⁻³ sodium hydrogen carbonate. The scavenger for the suppressor was 1.5×10⁻² mol dm⁻³ sulfuric acid. Flow rates of both the eluent and the scavenger were 2 cm³ min⁻¹. The injection volume of a sample solution was 0.1 cm³. The concentration of nitrate ions in the sodium nitrite solution was determined by means of the calibration-curve method. Intensity of each nitrate signal was obtained as an integrated value after deducting a base line or a foot of nitrite signal. The ion chromatogram of the filtrate in the nitron method for potassium nitrate was also measured.

Results and Discussion

Nitrate

The analytical results for the reagent potassium nitrate obtained by the nitron method have been summarized in Table 1. By washing the precipitate in a glass-filter crucible with the cold saturated aqueous solution of nitron nitrate[13], the loss resulting from the washing process could be neglected. An obviously lower value was obtained when the precipitate was washed with cold water containing no nitron nitrate. The solubility of nitron nitrate in water has been reported as 0.099 g dm⁻³ at *ca.* 20°C[26,27], 0.31 g dm⁻³ at 25°C[28], a value between 0.371 and 0.531 g dm⁻³ at 20°C[13], or 0.49 g dm⁻³ at 20°C[29]: there exists some discrepancy in these values. Since the solubility of nitron nitrate is not so large and the volume of the cold

Table 1   Results of gravimetry of nitrate ion

Sample	Purity[a], wt%	Purity[b], wt%
KNO₃	99.61±0.04 (*n*=6)	99.71±0.07
KNO₃	99.55±0.04 (*n*=5)[c]	99.65±0.07
HNO₃	99.90±0.06 (*n*=5)[c,d]	

a. ± indicates the relative standard deviation for each mean value; *n* is the number of measurements.
b. Values after the correction on the basis of the gravimetry for the nitric acid solution.
c. The two values were simultaneously obtained in parallel.
d. The value (mol percentage) relative to the concentration obtained by the coulometric titration.

washing solution left behind in the precipitation is very small, the quantity of the nitron nitrate introduced from the solution is negligible. The amount of the adsorption moisture on the surface of a glass-filter crucible slightly changes according to the atmosphere in which one weighs the crucible. The change of the weight of the moisture is, however, canceled by subtracting a blank value. The blank values with potassium hydroxide were in good agreement with those without potassium hydroxide: no additional nitrate was introduced from the hydroxide.

Though the nitron-method gravimetry is an absolute method, there are some possibilities for systematic error: these questions include whether the nitron used contains impurities which react with nitrate ion in a similar way to nitron, whether the solubility of nitron nitrate under the experimental condition of precipitation is not so small, whether vaporization as the form of nitric acid happens during the heating. To examine these possibilities, a high purity nitric acid which had been determined by an acidimetric coulometric titration was analyzed by the nitron method in parallel with the potassium nitrate solution simultaneously. The concentration of the $ca.$ 0.08 mol kg^{-1} nitric acid prepared from a high purity nitric acid was determined to be (8.1233± 0.0007)×10^{-2} mol kg^{-1} (8 determinations) with the coulometric titration cell equipped with two center compartments, where no loss of sample from the generator-electrode chamber to the counter-electrode one was introduced. Though nitric acid has a possibility of containing nitrous acid, judging from the redox reaction between potassium permanganate and nitrite ions we confirmed that nitrous acid in the nitric acid used was

within 0.003% (mole ratio) relative to nitric acid. The analytical result for the nitric acid solution by the nitron method has also been represented in Table 1. Since the result nearly agrees with the concentration obtained by the acidimetric coulometric titration, no systematic error was caused by the above-mentioned possibilities. But it is desirable to correct the difference (0.10±0.06%) of the result for the nitric acid solution from 100%, as also indicated in Table 1.

The nitrate ions left in the filtrate were found from the ion chromatogram (Fig. 3) to be 0.28% of the total ones under the experimental conditions. Because of the so-called salt effect[30], the value of 0.28% seems to be much larger than that expected from the solubility of nitron nitrate. Only 0.10±0.06% was, however, enough to correct the result of the gravimetry as described above. As has been suggested since the beginning of the nitron method[12,15,27,31], some component in the mother liquor may have been occluded to compensate, to some extent, for the nitrate ions left in the filtrate.

Nitrite

Permanganate ion has a sufficient ability to oxidize nitrite ion to nitrate ion in an acidic solution, as the following equation shows:[32,33]

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$$
$$2Mn^{2+} + 5NO_3^- + 3H_2O. \quad (2)$$
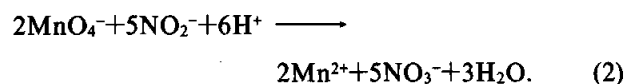
The sample solution of nitrite ions must be added under the surface of the excess potassium permanganate solution to prevent nitrous acid from vaporizing. Permanganate ions in the presence of manganese(II) ions tend to form brown precipitate of manganese(IV) oxide[34], though this reaction is not so fast under the acidic condition in the present paper:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2\downarrow + 4H^+. \quad (3)$$
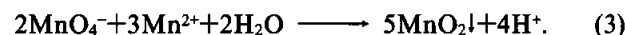
Therefore, the excess quantity of potassium permanganate was immediately reduced to manganese(II) ion by a slight excess of 0.05 mol dm^{-3} sodium oxalate solution. Since oxalate ions interfere with the nitron-method gravimetry[11,26,35], the excess oxalate ions were decomposed by an extremely slight excess of 0.02 mol dm^{-3} potassium permanganate. The remaining potassium permanganate could be reduced with 2.0 mol dm^{-3} formic acid solution. Formic acid does not interfere with the nitron method.[14] If the excess permanganate ions were reduced by only formic acid without sodium oxalate, the brown precipitate of manganese(IV) oxide would be undesirably formed before formic acid reacted with permanganate ions. Though bromine could oxidize nitrite ions to nitrate ions in a neutral solution, unfortunately the bromide ions formed introduced a positive error in the nitron method.

The analytical result for the reagent sodium nitrite obtained by the permanganate oxidation-nitron method
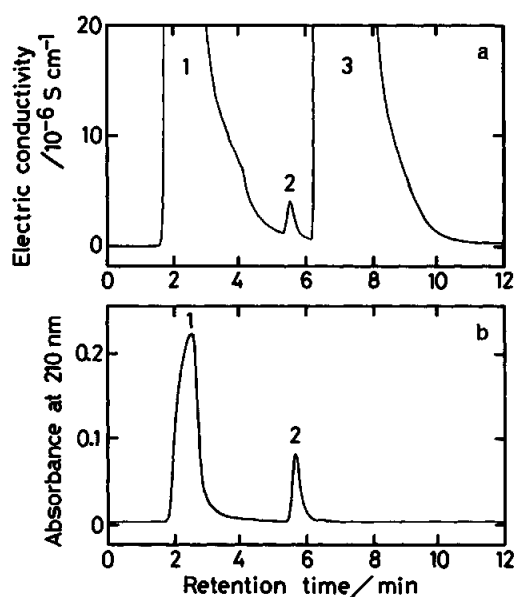

Fig. 3 Ion chromatogram of the filtrate in the nitron method for potassium nitrate. Column temperature: 40° C; (a) electric conductivity; (b) absorbance at 210 nm; 1; acetate ion peak; 2: NO$_3^-$ peak; 3: SO$_4^{2-}$ peak.

is indicated in Table 2. The value includes sodium nitrate existing as an impurity in the reagent sodium nitrite: the value has been estimated on the assumption that all nitrate ions in the precipitate of nitron nitrate resulted from nitrite ions themselves. The analytical result for the reagent potassium nitrate obtained by the permanganate oxidation in parallel with the reagent sodium nitrite (Table 2) agrees with the result without potassium permanganate tabulated in Table 1. Consequently, we have experimentally proved that the permanganate oxidation described in the procedure of Experimental section does not interfere with the nitron-method gravimetry.

Though the nitrate ions in the presence of nitrite ions can be determined by the nitron method after the decomposition of only nitrite ions with hydrazine hydrosulfate[11], the small quantity of nitrate ions in the reagent sodium nitrite could be determined easily by ion chromatography without any pretreatment. A

Table 2 Results of gravimetry with permanganate oxidation

Sample	Purity[a], wt%	Purity[b], wt%
NaNO$_2$	99.83±0.07 (n=3)[c,d]	99.93±0.09[d]
KNO$_3$	99.65±0.11 (n=3)[c]	99.75±0.13

a. ± indicates the relative standard deviation for each mean value; n is the number of measurements.
b. Values after the correction on the basis of the gravimetry for the nitric acid solution.
c. The two values were simultaneously obtained in parallel.
d. Apparent value containing nitrate ions in the reagent sodium nitrite. See text for the true purity.
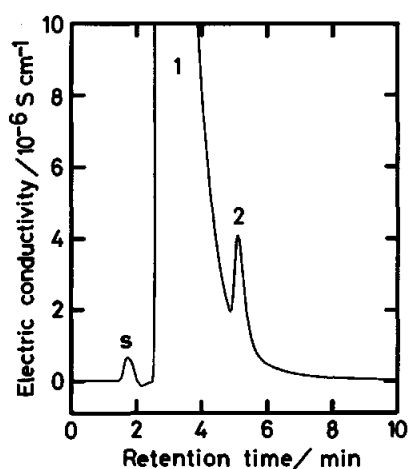

Fig. 4 Ion chromatogram of nitrate ions in the presence of a large amount of sodium nitrite. Sample: 1-kg aqueous solution containing 1.4985 g of the reagent sodium nitrite; column temperature: 45°C; 1: NO$_2^-$ peak (the electric conductivity at the top is 525.7 µS cm^{-1}); 2: NO$_3^-$ peak; s: this peak seems to result from the many sodium ions in the sample solution.

typical ion chromatogram of a sodium nitrite solution is shown in Fig. 4. The nitrate signal was extracted by subtracting the foot of the nitrite signal with use of a least-squares method. A calibration curve was depicted with the above-mentioned potassium nitrate, of which the purity had been determined. The nitrate ions contained in the reagent sodium nitrite were 0.45±0.01 wt% as NaNO$_3$. The value is constant for 80 d at least after the preparation of the sodium nitrite solution, if the solution is kept in a cool and dark place.[36] From both the quantity of nitrate ions in the reagent sodium nitrite and the analytical result of the reagent by the gravimetry given in Table 2, the true purity of nitrite ion itself in the reagent sodium nitrite was estimated to be 99.57±0.09 wt% (99.47±0.07 wt% before the correction on the basis of the gravimetry for the nitric acid solution) in consideration of the difference between the chemical formula weight of sodium nitrite and that of sodium nitrate. The sum of both sodium nitrite and sodium nitrate in the reagent sodium nitrite was recalculated to be 100.02 wt% (99.92 wt% before the correction on the basis of the gravimetry for the nitric acid solution).

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