

DEVELOPMENT OF PROTOCOL FOR ANALYSIS OF ACID NITRATING MIXTURE

Andriana SURLEVA^{1*}, Gabriela ATANASOVA¹, Iliana BACHEVA¹,
Georgi CHERNEV², Mustafa Mohd Al Bakhri ABDULLAH³
Stela GEORGIEVA¹

¹Analytical Chemistry dep, University of Chemical Technology and Metallurgy, 8 “Kl. Ohridski” blvd., 1756 Sofia, Bulgaria, e-mail: surleva@uctm.edu

²Silicate Technology dep, University of Chemical Technology and Metallurgy, 8 “Kl. Ohridski” blvd., 1756 Sofia, Bulgaria, e-mail: g.chernev@uctm.edu

³Faculty Engineering Technology (FETech), University of Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, Taman Muhibbah, 02600 Jejawi, Perlis, Malaysia, e-mail: mustafa_albakri@unimap.edu.my

Abstract

Technological control of nitration of organic compounds needs data about a composition of acid nitrating mixture before and after nitration. Content of water is a crucial factor for efficiency and safety of the nitration process. The industrial laboratories demands for fast, accurate, precise, low cost and easy to maintain analytical methods. This paper presents the development of a protocol for determination of composition of acid nitrating mixture. The determination of nitric acid is based on redox back titration. Determination of sulfuric acid is based on direct precipitation titration. Water content is determined by calculation. The proposed method showed good accuracy, precision and selectivity, with recoveries (99.80±0.06)% H₂SO₄ and (98.91±0.80)% HNO₃, and total analysis time 20 min..

Keywords: acid nitrating mixture, composition determination, nitric acid, sulfuric acid, titration

Introduction

Nitrocellulose has a wide range of applications: surface finishing, chemical admixture, printing inks, varnishes, adhesives, explosives [1-3]. In a Bulgarian factory nitrocellulose is produced by a classical nitrating procedure with a mixture of nitric and sulfuric acids [3-5]. The composition of acid nitrating mixture determine the extent of esterification and hence the quality of the obtained product [3,6]. The control and optimization of technological process use data about the composition of nitrating mixture. Quantity of water obtained during the nitration process is a crucial factor for efficiency and safety of the process. Hence, reliable and accurate information about the composition of nitrating mixture should be provided as fast as possible.

Modern analytical methods for nitrates and sulfates determination offer high sample throughput and automatization [7-9]. However, they are suitable for determination of low concentrations and serial dilutions are needed when major components are determined. A line of titrimetric and gravimetric methods for sulfate or nitrate determination are also reported, but interference from nitrate ions needs a separation procedure to be included [9,10].

This study is aimed at developing of protocol for determination of composition of acid nitrating mixtures. The developed analytical method should meet the following criteria: good

* Corresponding author: surleva@uctm.edu

accuracy and precision, as low as possible sample pretreatment, wide working concentration range, low cost and easy to maintain instruments, and easy implementation in automatic analytical devices.

Materials and Methods

Reagents and instrumentation

Standard solution of $K_2Cr_2O_7$ (0.01667 mol/l) was prepared by weighing 4.9010g $K_2Cr_2O_7$ (p.a.) and dilution up to 1 L water in measuring flask. For preparation of $FeSO_4$ solution 46 g $FeSO_4 \cdot 7H_2O$ (p.a.) were dissolved in 10 mL conc. HCl and 100 mL d. H_2O . The obtained solution was diluted up to 500 mL Ferroin (0.0025 mol/L) and dithizone – saturated solution in acetone, were used as indicators. Standard solution of $Pb(NO_3)_2$ (0.1000 mol/L) was used. Boeco combined pH electrode was used for potentiometric measurement of pH. Automatic burette (Metrohm) was used for the titration.

Procedures

Determination of sulfates: mix 5 mL sample solution with 50 mL acetone, adjust pH to 2 by adding NaOH (pH is controlled potentiometrically). Add 10-15 drops of indicator solution. Titrate with $Pb(NO_3)_2$ solution till first color change. Prepare a reference sample by adding 5 mL standard solution of H_2SO_4 , add 50 mL acetone, adjust pH with NaOH solution, add the indicator and titrate with $Pb(NO_3)_2$ standard solution till the first color change.

Determination of nitrates: 3 mL sample solution with 5.00 mL $FeSO_4$ solution, add 15mL concentrated H_2SO_4 . Boil the mixture for 3 min, cool and add 20 mL H_2O and 1mL Ferroin solution. Titrate with $K_2Cr_2O_7$ standard solution till color changes from red to blue. Prepare and titrate a blanc sample.

Analysis of real sample: Acid nitrating mixture is filtered using glass filter and diluted 1:100 with d. H_2O . An aliquot of 5 mL of diluted solution was taken for sulfate determination. An aliquot of 3 mL was taken for nitrate determination.

Results and Discussion

Determination of sulfuric acid in a mixture of H_2SO_4 and HNO_3

A method based on titration with $Pb(NO_3)_2$ in acetone/water medium was chosen to be studied for application in analysis of acid nitrating mixture [11,12]. A model sample containing H_2SO_4 and HNO_3 (1:1) in concentration 0.05 M each was prepared. The sample aliquot was mixed with acetone; apparent pH 2 was adjusted with NaOH solution. Dithizone was used as an indicator and an aqueous solution of $Pb(NO_3)_2$ – as a titrant. To ensure complete precipitation of $PbSO_4$ the acetone/water ratio shouldn't change considerably during the titration. In this experiment the acetone in a solvent mixture was 90% at the beginning and 80% at the end of the titration. The color transition of the indicator was not sharp enough to ensure accurate detection of the equivalence point. To overcome this limitation, the end of titration was determined at the first color change of the indicator and a reference sample of standard solution of H_2SO_4 was titrated along with the model sample. The results were calculated using the equations:

$$C_{Pb^{2+}} \cdot V_1^{eq} - C_{SO_4^{2-}}^{ref} \cdot V_{ref.sample} \quad (1)$$

$$C_{Pb^{2+}} \cdot V_1^{eq} = C_{SO_4^{2-}}^{ref} \cdot V_{ref.sample} \quad (2)$$

$$\frac{V_1^{eq}}{V_2^{eq}} = \frac{C_{SO_4^{2-}}^{ref}}{C_{SO_4^{2-}}^x} \quad (3)$$

$$C_{SO_4^{2-}}^x = C_{SO_4^{2-}}^{ref} * \frac{V_2^{eq}}{V_1^{eq}} \quad (4)$$

$$m_{H_2SO_4} = C_X * V_{sample} * M_{H_2SO_4} \quad (5)$$

$C_{SO_4^{2-}}^{ref}$ - concentration of sulphate ions in the reference sample; $C_{SO_4^{2-}}^x$ - unknown concentration; V_1^{eq} - volume consumed in the titration of sulfate ions in the reference sample; V_2^{eq} - volume consumed in the titration of sulfate ions in the sample; $V_{ref.sample} = V_{sample}$

Determination of sulfate in a model mixture of sulfuric and nitric acids (1:1) by the developed method showed recovery of (99.80±0.06)% (n=6, P=95%). The total concentration of acid mixture was 0.1 M. At higher concentrations of model samples (0.2 M) the quantity of formed precipitate increased and hindered the observation of equivalence point.

Two problems with sulfate determination in acid nitrating mixture could be noted. First, H_2SO_4 in acid nitrating mixture is in high concentrations. Second, H_2SO_4 and HNO_3 are at the same order of concentration. Usually, a separation procedure or ion chromatography are used for sulfuric acid determination. On the one hand, using high sensitive methods with short working range for determination of major components (as ion chromatography) needs serial dilutions and thus lowers the precision and accuracy of analytical results. On the other hand, a complicated sample pretreatment for separation of major components prolongs analysis time and could deteriorate the quality of the results as the risk of incomplete separation, loss of analyte or adding impurities by the used reagents is increased. The most studied methods for sulfate determination are based on titration or gravimetric determination with barium salt [10,13]. However, in these methods high interference from nitrates is reported as the solubility of formed $BaSO_4$ increases in nitrate containing medium. To ensure complete precipitation, organic solvents are used. A titration with $Pb(NO_3)_2$ in acetone/water medium and dithizone as an indicator was described [11,12]. The advantage of the method was determination of sulfate in the presence of nitrate ions; however only results from determination of low sulfate concentrations were reported as formed precipitate interfered with used spectrophotometric detection. The method was the base for the development of the modified protocol proposed in this work. To wider the working range and to improve the accuracy of determination of high sulfate concentrations a visual indication of equivalence point and a reference sample titration were applied. The proposed protocol allowed determination of high concentrations of sulfate (0.05 M) in a 1:1 mixture of nitric and sulfuric acids.

Determination of nitric acid in a mixture of H_2SO_4 and HNO_3

The modified Leight's method for determination of nitrate was used [10,14,15]. The method offered determination of nitrate in sulfuric acid medium and was based on a redox back titration. $FeSO_4$ was added to the sample solution. After the reduction of nitrate ions in H_2SO_4 medium and boiling, the unreacted $FeSO_4$ was titrated with primary standard solution of $K_2Cr_2O_7$ and ferroin as an indicator. Blanc sample was titrated along with the sample solution. The method offered two advantages: determination of nitrate in sulfuric acid medium and skipping of standardization of $FeSO_4$ solution.

The results were calculated using the equation:

$$m_{HNO_3} = 2 * C_{K_2Cr_2O_7} * (V_{K_2Cr_2O_7}^{blanc} - V_{K_2Cr_2O_7}^{sample}) * M_{HNO_3} * 10^{-3} \quad (6)$$

A model sample containing H_2SO_4 and HNO_3 (1:1) in concentration 0.1 M each was used in this study. In the Leight's method interference from chloride ions was reported when low concentrations of nitrate ions were determined. To check the interference at high concentrations of NO_3^- , the titration was performed with and without addition of NaCl to model samples (5 g NaCl/5 mL sample). The results from both titrations coincided; hence, chloride was not interfering. Determination of nitric acid in a model mixture of H_2SO_4 and HNO_3 (1:1, 0.2 M total concentration) showed recovery of $(98.91 \pm 0.80)\%$ ($n=7$, $P=95\%$) with relative error of -1.1% and relative standard deviation of 0.91%.

Protocol for determination of the composition of acid nitrating mixture

Acid nitrating mixture consists of conc. HNO_3 , conc. H_2SO_4 and some water formed during the nitration process. The proposed protocol for determination of the composition of acid nitrating mixture is presented on Fig.1. The sulfuric acid content was determined by direct precipitation titration. The content of nitric acid was determined by back redox titration. Water content was determined by calculation.

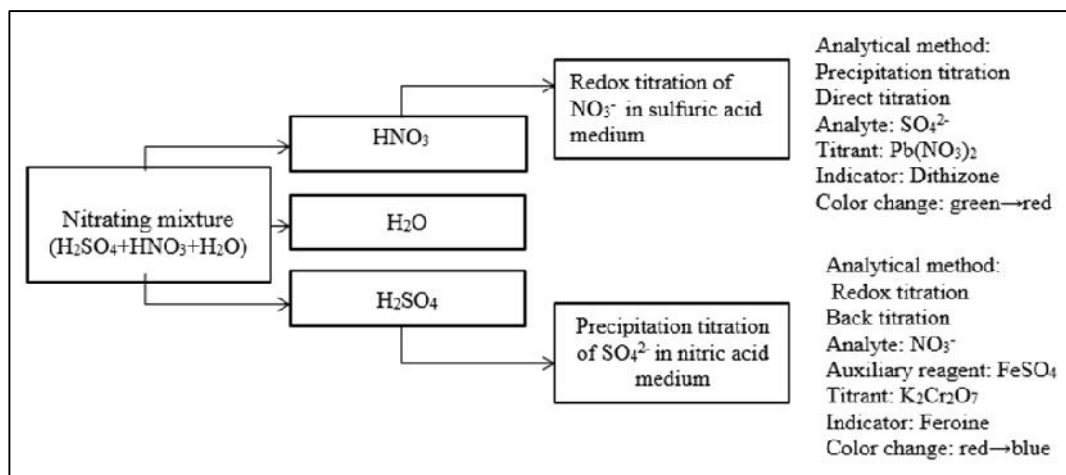


Fig. 1. Protocol for analysis of acid nitrating mixture

Analysis of real samples

The results from analysis of real samples from nitration of cellulose in Bulgarian factory are presented in Table 1. For comparison the results from factory laboratory are also presented. The standard method includes the following stages: (1) determination of total acidity by acid-base direct titration with secondary standard solution of NaOH; (2) sample treatment for separation of nitric and sulfuric acid by heating for 2 hours at $700\text{ }^\circ\text{C}$; (3) direct titration of sulfates with barium salt; (4) calculation of nitric acid content from total acidity and sulfuric acid content; (5) calculation of water content from the data for nitric acid and sulfuric acid.

Table 1. Analysis of real samples of acid nitrating mixture

Components	Real sample, %	
	this method (n=6, P=95%)z	standard method (n=3, P=45%)
Nitric acid	48.2±0.4	47.9±2.1
Sulfuric acid	51.0±0.3	51.8±0.7
Water	0.81	0.07

The data presented in the table showed that the results from two methods statistically coincided in the frame of their confidence intervals.

Conclusion

The standard method for the determination of the composition of acid nitrating mixture used in the factory laboratory suffers from the following drawbacks: (a) time-consuming and laborious sample pretreatment for nitric acid removal; (b) indirect determinations of nitric acid and water content by calculations which make the determination unreliable and highly influenced by systematic and random errors.

The protocol for determination of the composition of acid nitrating mixture proposed in this work is based on determination of nitrate ions in sulfuric acid medium and determination of sulfate ions in a nitrate containing medium, which allowed the separation of components to be skipped. The analysis time was considerably shortened: from more than 2 hours in classical procedure down to 20 min in this method. The content of nitric and sulfuric acids was determined as a result of titration procedures which improved the reliability of the data compared to the calculation of nitric acid in classical method. As a result of direct determination of nitric and sulfuric acids, the results about water content were more reliable and accurate. Additionally, low cost and easy to maintain instruments are used. The developed protocol could be implemented in automatic titration devices and the study is currently in progress in our laboratory.

Acknowledgements

The financial support of the Science and Research program of UCTM (project11597/2016) is gratefully acknowledged. We are grateful to Mr. Varban Pechkov (Arsenal AD, Kazanluk, Bulgaria) for the idea, valuable discussions and support that he gave to this work.

References

- [1] ***, Wolff Cellulosics - Bayer Materialscience, *Nitrocellulose – Applications, Characterisation, Production and Storage* - Supplier Data, <http://www.azom.com/article.aspx?ArticleID=2785> (2013)
- [2] ***, Dow Wolff Cellulosics, Nitrocellulose, Essential for an Extra-Special Finish, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08a6/0901b803808a680d.pdf?filepath=/822-00007.pdf&fromPage=GetDoc
- [3] R. Meyer, J. Köhler, A. Homburg, **Explosives**, 6th Ed., Axel Homburg, Wiley-VCH & Co. KGaA, Weinheim, 2007, p. 220.

-
- [4] G. Yan, M. Yang, *Recent advances in the synthesis of aromatic nitro compounds*, **Org. Biomol. Chem.** **11**, 2013, pp. 2554-2266.
- [5] A. A. Kulkarni, *Continuous flow nitration in miniaturized devices*, **Beilstein J. Org. Chem.** **10**, 2014, pp. 405-424.
- [6] M. López-López, J.M. R. Alegre, C. García-Ruiza, M. Torre, *Determination of the nitrogen content of nitrocellulose from smokeless gunpowders and collodions by alkaline hydrolysis and ion chromatography*, **Anal. Chim. Acta** **685**, 2011, pp. 196-203.
- [7] M. R. Baezzat, G. Parsaeian, M. Ali Zare, *Determination of traces of nitrate in water samples using spectrophotometric method after its preconcentration on microcrystalline naphthalene*, **Quim. Nova** **34**, 2011, pp. 607-609.
- [8] J.A. Morales, L.S. de Graterol, J.Mesa, *Determination of chloride, sulfate and nitrate in groundwater samples by ion chromatography*, **J Chromatogr A.** **884**, 2000, pp.185-90.
- [9] B. López-Ruiz, *Advances in the determination of inorganic anions by ion chromatography*, **J Chromatogr A.** **881**, 2000, pp. 607-627.
- [10] W.J. Williams, **Handbook of Anion Determination**, Butherworths, London 1979 (Russian edition, ,) 1982, pp. 525-536.
- [11] Metrohm, Application bulletin 140/4e, *Titrimetric determination of sulfate*, Method 4, pp. 8-10.
- [12] D.C. White, *The titrimetric microdetermination of sulphate using lead nitrate as titrant and dithizone as indicator*, **Mikrochimica Acta** **47**, 1958, pp. 254-269.
- [13] M. Lugowska, E. Stryjewska, S. Rubel, B. Ostrowska, *Comparison of volumetric methods of sulphates determination in water and waste*, **Chemia Analityczna** **37**, 1992, pp. 551-557.
- [14] G. Latimer, O. Chamber, *A modification of Leight's for determining nitrate*, **Talanta** **12**, 1965, pp. 417-423.
- [15] C. Henner-Wirguin, D. Friedman, *Effect of chloride ions on the determination of nitrate by Leith's*, **Talanta** **7**, 1960, pp. 121-123.
-

Received: October 14, 2016

Accepted: September 17, 2016