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ASSAY OF NITRO AND NITROSO COMPOUNDS BY SOLUTION THERMOCHEMISTRY

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Some nitro and nitroso compounds have been determined by direct reduction with Ti(III) chloride without the necessity for degassing the analyte solutions. Methods have been developed for the determination of some binary mixtures by both enthalpimetry and catalytic thermometric titrimetry. The accuracy at the 0.1 mMole level is ±1%, and the time taken for a single titration is less than 2 minutes.

Since the introduction of organic nitro and nitroso compounds into explosive and chemical pesticide industries, many attempts have been made to effect a general and rapid method for their assay. Methods used so far include classical volumetry [1], gravimetry [2], and indirect thermometry [3]. None of these methods can be used without degassing the sample solutions, hence the time of a determination is generally too long. We have been able to assay some nitro and nitroso aromatic compounds by direct reduction with titanium(III) chloride without degassing the sample solutions at room temperature. Methods have been developed for the determination of some binary mixtures by both enthalpimetric injection and catalytic thermometric titrimetry. The accuracy at 0.1 mMole level is ±1% and the time taken for a single titration was less than two minutes.

Experimental

Apparatus

The apparatus used, which was designed by Bark, has been previously described [4]. The working volume of the prepared samples was fixed at 10 cm^3 and the amount of titanium(III) chloride injected was constant and contained in a fixed volume (0.5 cm^3) of reagent solution. The recorder used to measure the heat pulse, manifested as an off-balance voltage from the Wheatstone Bridge circuit, was capable of recording from 1 mV to 5000 mV for a FSD of 200 mm per deflection. The determination were carried out in a temperature-controlled room at 23°.

Procedure

The stock solutions (10 mMole) of nitro compounds were prepared by dissolving the appropriate amounts in 50 cm^3 glacial acetic acid and made to the standard mark with distilled water. Series of calibration solutions (0.00–0.1 mMole), each containing 10.0 cm^3 of 60% w/v potassium citrate and adjusted to the standard mark with distilled water, were prepared. 10.0 cm^3 of each of these solutions was pipetted into the titration vessel. The submersive pipette was filled with titanium(III) chloride to the pre-calibrated mark, rinsed with distilled water. The titration vessel, containing a magnetic follower and covered with a polyethylene cap, that housed the submersive pipette and thermistor was placed in the insulation block. The solution was stirred magnetically for one minute until thermal equilibrium was attained. The nitro compounds were then titrated against 1M titanium(III) chloride solution of lower case zero heat of dilution at 10 mV FSD and a chart speed of 120 mm per minute. Determinations were also carried out with degassing the solutions with carbon dioxide and the result compared.

Results

The results of the determinations of some nitro and nitroso compounds are listed in Tables 1 and 2. The accuracy was found to be ±1% and the time of a determination of any one nitro compound was less than two minutes. With the polynitro compounds, especially picric acid, higher amounts of potassium citrate solution must be added to ensure that the reaction goes to completion at room temperature.

Assay of binary nitro compound mixtures

All nitro compounds react with titanium(III) chloride and iron(II) sulphate, but only a few react as an acid in non-aqueous medium. Nitrobenzene and 1,3-dinitrobenzene can be reduced by Ti^{3+}, but only 1,3-dinitrobenzene can be titrated in non-aqueous medium as acid with alcoholic potassium hydroxide.

By using the concept of partial molar heat pulse and non-selective reactions, as proposed by Bark and Nya [5], binary mixtures of nitro compounds have been determined and the result is as shown in Table 2.

Conclusion

Procedures for the determination of aromatic nitro and nitroso compounds with titanium(III) chloride, without degassing the sample solution, are described. The method is rapid and good enough for routine work. The technique is very simple and

no special apparatus is required for titanium(III) chloride storage. Standardization of the titrant is not necessary.

Table 1 Assay values of some nitro and nitroso compounds

Amount (mMole) in 10 cm^3 taken	Amount (mMole) recovered without degassing the solutions	Amount (mMole) recovered with degassing	% Recovery
Nitrobenzene			
0.040	0.040	0.0398	100
0.060	0.06(1)	0.060	100.2
2-Nitrophenol			
0.040	0.040	0.040(1)	100
0.060	0.060	0.060(7)	100
2,4-Dinitrophenol			
0.040	0.0399	0.040(2)	99.8
0.060	0.060(1)	0.060	100.2
2,4,6-Trinitrophenol			
0.02	0.020(2)	0.020	101
0.04	0.0399	0.040	99.8
4-Nitrosophenol			
0.04	0.040	0.0396	100
0.06	0.060	0.0598	100
2-Nitroso-1-naphtol			
0.04	0.040	0.040	100
0.06	0.060(5)	0.0599	100.8
1-Nitroso-1-naphtol			
0.04	0.040	0.04(1)	100
0.06	0.060	0.06(1)	100

Table 2 Assay values of some binary aromatic nitro compound mixtures

Amounts (mMole) of binary mixtures taken			Amount (mMole) of each component recovered)	
Nitrobenzene	0.020	0.040	0.0198	0.0388
+	+	+		
1,3-Dinitrobenzene	0.100	0.080	0.10(1)	0.0797
4-Nitro-anisole	0.020	0.060	0.020(6)	0.060(5)
+	+	+		
2,4-Dinitro phenol	0.100	0.060	0.1025	0.0596
3-Nitro-phenol	0.080	0.060	0.0795	0.0595
+	+	+		
2,4,6-Trinitro phenol	0.020	0.030	0.020(3)	0.0278

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Zusammenfassung – Einige Nitro- und Nitrosoverbindungen wurden durch direkte Reduktion mit Ti(III)-chlorid bestimmt, ohne dass die Notwendigkeit der Verdampfung der Analysenlösung besteht. Es wurden Methoden zur Bestimmung einiger binärer Gemische durch Enthalpimetrie und katalytische thermometrische entwickelt. Die Genauigkeit beträgt im Bereich von 0.1 mMol ±1%, und eine Titration erfordert weniger als 2 Minuten.

Резюме – Некоторые нитро- и нитрозосоединения были определены прямым восстановлением с треххлористым титаном без необходимости дегазации анализируемых растворов. Разработаны методы определения некоторых двойных смесей с помощью энтальпиметрии и каталитической термометрической титриметрии. Точность метода при концентрации 0,1 ммоля составляла ±1%, а время, необходимое для одного титрования 2 минуты.