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Vanadametric Determination of p-Phenylene Diamine

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Monoamines are estimated by titration with a standard solution of sodium nitrite while m-diamines are determined by titration with a standard solution of a diazo compound. Neither of these methods is useful for the determination of p-phenylene diamine. The older methods for the determination of this substance depend on its oxidation with dichromate in the presence of aniline to form an indamine. The method is highly sensitive to changes of temperature, dilution, speed of addition of dichromate, etc. Besides, aniline itself undergoes oxidation to a certain extent.

Meldola and Evans[8] suggested estimation of p-phenylene diamine through oxidation with dichromate and determining the ammonia evolved. Green and Johnson[4] treated p-phenylene diamine with an excess of lead peroxide in sulfuric acid solution. The excess of lead peroxide was destroyed with oxalic acid and the benzoquinone formed was treated with potassium iodide. The iodine liberated was treated with standard sodium thiosulphate solution. The results obtained by this method were five percent lower than the theoretical, evidently due to further oxidation of some of the resulting quinone by lead peroxide.

Heiduschka and Goldstein[5] have made use of the Krause-reaction where p-phenylene diamine was converted into benzoquinone dichloroimide $C_6H_4(NCl)_2$ by the action of a solution of calcium hyperchlorite. The quinone dichloroimide formed was estimated by reduction with stannous chloride. The method failed to yield stoichiometric results and corrections were found to be necessary. Callan and Henderson[2] attempted the estimation of p-phenylene diamine by converting it quantitively into its water-insoluble acetyl derivative but even here the results obtained were found to be consistently low. The same authors have applied the method due to Effront[3] for the estimation of p-phenylene diamine. They found that in the presence of sodium carbonate, p-phenylene diamine can be estimated by treating a known quantity with excess sodium hypochlorite solution and titrating the excess with standard sodium arsenite using starch-iodide test papers as external indicator.

Herd[6] treated a suitable amount of p-phenylene diamine with alkaline 5% sodium hypochlorite solution and after destroying the excess reagent with sodium arsenite solution they extracted the quinone dichloroimide with chloroform. The chloroform extract was treated with potassium iodide and hydrochloric acid and the iodine liberated titrated with standard sodium thiosulfate solution. Bogdanov and Sukhobokova[1] have titrated p-phenylene diamine amperometrically in 100 ml of 2 N sulfuric acid with ceric sulfate using a rotating platinum electrode.

The author has now investigated the use of sodium vanadate for the estimation of p-phenylene diamine. The reaction between p-phenylene diamine and vanadate has been found to be slow, so that a direct titration of the substance was not possible even at a high acid concentration. The author has however observed that the estimation can be successfully carried out by an indirect method, namely adding excess sodium vanadate and titration of the excess with standard ferrous sulfate solution. In this indirect method the oxidation of p-phenylene diamine has been found to be complete within five minutes when the solution was only 1 N with respect to sulfuric acid. The results of the author's experiments are summarised in Table 1.

Table 1

20 ml of about 0.05 N sodium vanadate solution + sulfuric acid + water to make up to 50 ml + 10 ml of p-phenylene diamine solution. The oxidant left over after the prescribed length of time is back titrated with ferrous sulfate solution. (Amount of p-phenylene diamine taken = 0.1245 millimols)

Overall concentration of sulfuric acid	Millimols of p-phenylene diamine found by vanadate method	
	5 min reaction	15 min reaction
1.0 N	0.1244	0.1239
2.0 N	0.1239	0.1244
4.0 N	0.1241	0.1239
6.0 N	0.1239	0.1244

It will be seen from Table 1, that p-phenylene diamine is quantitatively oxidised in five minutes, even in the cold, when it is treated with excess sodium vanadate.

The author has carried out a large number of estimations of p-phenylene diamine by the method now developed and found that the vanadametric method gives results which are in close agreement with the theoretical. Table 2 shows some typical results obtained by the author.

Table 2

Millimoles of p-phenylene diamine taken (ceric sulfate method)	Millimoles of p-phenylene diamine found (new vanadametric method)
0.0622	0.0620
0.1245	0.1239
0.2257	0.2263
0.2880	0.2891
0.3123	0.3117

Summary

p-Phenylene diamine can be determined by adding an excess of sodium vanadate solution to the sample and back-titrating with ferrous sulfate solution. Good results are obtained.

Zusammenfassung

Eine Methode zur Bestimmung von p-Phenylendiamin beruht auf Zusatz überschüssiger Natriumvanadatlösung und Rücktitration mit Eisen(II)-sulfatlösung. Es werden gute Ergebnisse erzielt.

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Spektralphotometrische Bestimmung von Acrylnitril neben Styrol

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Mit 2 Textabbildungen

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Die Bestimmung von Acrylnitril mit Dodecanthiol[1] liefert bei kleinen Acrylnitrilgehalten sehr ungenaue Ergebnisse. Bei Gegenwart von ungesättigten Verbindungen wie z. B. Styrol war eine quantitative Erfassung nicht mehr möglich. Es wurde daher nach einer Methode gesucht, die es gestattet, kleine Mengen an Acrylnitril neben einem Überschuß an Styrol zu bestimmen.

Erfolgversprechend schien eine spektralphotometrische Bestimmung, da das UV-Spektrum des Acrylnitrils zwischen 200 und 220 nm eine scharfe Absorption zeigt. Da Styrol in diesem Bereich ebenfalls eine starke Absorptionsbande besitzt, deren Maximum die gleiche Lage hat wie das Maximum der Acrylnitril-Bande, mußte ein zweiter Bereich mit möglichst starker Absorption hinzugezogen werden. Hierfür geeignet schien der Bereich zwischen 240 und 250 nm.

Abb. 1 gibt die UV-Spektren von Acrylnitril und Styrol in Methanol wieder. Danach besitzen Acrylnitril und Styrol eine scharfe Bande bei 204 nm. Bei 247 nm liegt das Maximum einer weiteren schwächeren