tate standard, arabinose tetraacetate, and sorbitol hexaacetate by direct saponification and by the proposed method are in good agreement and gave calculated values for these pure compounds.

Determination of acetyl in acetylated carbohydrate polymers is shown in Table II. The acetates of guar mannogalactan, araban, starch, and pectin gave results in good agreement with those obtained by saponification.

Table II. Determination of Acetyl in Acetylated Carbohydrate Polymers

	Acetyl, %		
Acetate	Colorimetric	Saponification	Calcd.
Glucose penta-	57.6 55.7 57.0	56.5	55.1
Guar tri-	47.5 45.2 46.9	47.3	44.8
Araban di-	41.3	41.7	39.8
Starch tri-	43.9	43.9	44.8
Pectin di-	37.3 35.3 36.6	[a]	33.1[b]

[a] Contains carbomethoxyl groups which saponify under same conditions as acetyl.

[b] Calculated on basis of 100% anhydrouronic acid.

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Complexometric Titrations Using Azoxine Indicators

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▶7 - (1 - naphthylazo) - 8 - quinolinol-5-sulfonic acid and several related compounds are valuable as metal ion indicators in complexometric titrations. Cadmium, cobalt, copper, lead, nickel, rare earths, thorium, yttrium, and zinc can be accurately titrated in acid solution with 0.05M (ethylenedinitrilo)tetraacetate. In many cases a small amount of copper must be present in order for the indicator to function properly. Calcium and magnesium do not interfere if the pH is 5.5 or less. With citrate as a masking agent, zinc and other divalent metals can be titrated in the presence of uranium(VI), thorium, or zirconium. The use of tartrate, fluoride, iodide, or thiourea as masking agents in certain cases also increases the selectivity of the method.

Compounds which form highly colored metal complexes are widely used as indicators for complexometric titrations of metal ions with (ethylenedinitrilo)tetraacetic acid (EDTA). Eriochrome Black T was the first such indicator to gain great popularity. It has been widely used for the titration of calcium and magnesium with EDTA, as well as for the direct titration of zinc, manganese, cadmium, and lead. It cannot be used for direct titration of metals such as copper, cobalt, and nickel because these metals react irreversibly with the indicator. Slight traces of iron and copper interfere with other titrations in which Eriochrome Black T is employed as the indicator.

Other indicators have been proposed for use in the titration of certain of the divalent metals. Murexide is reasonably good for copper and calcium, but is poor for zinc, cobalt, and the like. Pyridylazonaphthol (*1*) serves as an indicator for some titrations. Its chief disadvantage is its slow reaction in acid solution. Pyrocatechol Violet has been proposed as an indicator (*6*), but it does not seem to give a good color change for titration of divalent metals. Zincon (*5*) has been suggested as an indicator for EDTA titrations but information regarding its use is thus far sketchy. Aluminum (and probably several other metal ions) can be determined in an acidic water-acetone solution by adding excess EDTA and back titrating with zinc using dithizone indicator (*7*). This procedure works well if the pH is carefully controlled.

This paper is concerned with the analytical applications of a new class of metal ion indicators, the 7-(arylazo)-8-quinolinol-5-sulfonic acids, which will be called the azoxines for convenience. These indicators give sharp, easily detectable end points in the titration of a large number of metal ions. The titrations are carried out in moderately acid solution where calcium and magnesium do not titrate or interfere. Most of the titrations can be carried out in the presence of complexing anions such as tartrate, citrate, and sulfosalicylate. Finally, titrations using azoxine indicators lend themselves well to the use of masking agents to increase the selectivity of EDTA titrations.

PREPARATION AND PROPERTIES OF AZOXINES

The azoxine indicators were prepared by coupling a diazotized amine with 8-quinolinol-5-sulfonic acid. The product is purified by recrystallization from dimethylformamide and water.

Place 0.1 mole of the appropriate amine ground to a medium powder in a 1-liter beaker and add 50 ml. of water, 30 ml. of concentrated hydrochloric acid, and approximately 50 grams of crushed ice. When the amine solution has cooled to less than 10° C., add slowly a solution of 9 grams of sodium nitrite in 30 ml. of water through a funnel whose tip extends below the surface of the amine solution. Test for completeness of diazotization with starch-iodide paper.

While the mixture is still cold add 200 ml. of $1.2M$ sodium hydroxide. This should make the solution slightly basic (pH 8 to 10). Add with stirring 22.5 grams (0.1 mole) of lump-free 8-quinolinol-5-sulfonic acid. Stir 10 minutes and filter.

Dissolve the solid product in the minimum amount of warm (50° C.) dimethylformamide. Filter to remove any insoluble residue and add water to the filtrate equal to 2 or 3 times the volume of dimethylformamide used. Filter 3 or 4 hours later and dry in a vacuum desiccator.

The phenyl-, *p*-chlorophenyl-, *p*-nitrophenyl-, and 1-naphthylazoxines were prepared by this procedure. In dilute, acidic solution the phenyl derivative is orange-rose, the *p*-chlorophenyl is golden orange, the *p*-nitrophenyl is yellow-rose, and the naphthyl is rose-violet. These become gradually more yellow as the pH is raised, until at pH 8 they are almost clear yellow. The *p*-nitrophenylazoxine is an exception, becoming an intense rose-violet color in alkaline solution. All of these compounds form clear yellow complexes with copper(II), zinc, and several other metals. The absorption spectra for both free and complexed naphthylazoxine is given in Figure 1. Because in weak acid solution the color contrast between the free indicator and the metal complex is greatest in the case of naphthylazoxine, this compound was chosen as the most satisfactory indicator for visual titrations.

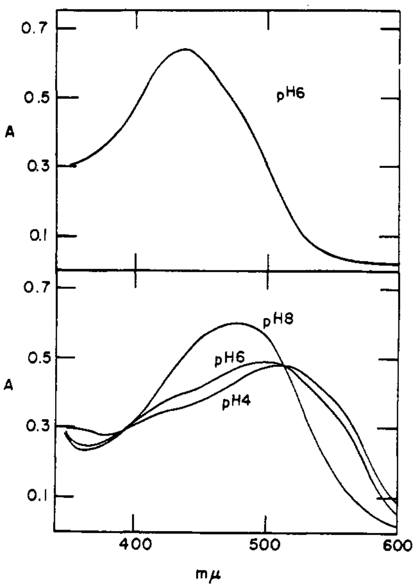

Figure 1. Absorption spectra

Upper curve. Complex of copper naphthylazoxine ($2 \times 10^{-6}M$)
Lower curves. Naphthylazoxine ($2 \times 10^{-5}M$)

REAGENTS AND APPARATUS

$0.05M$ EDTA. Prepare an aqueous solution from the reagent grade disodium or diammonium salt of (ethylenenitrilo)tetraacetic acid. Standardize by titrating zinc nitrate (pure zinc metal as primary standard) at pH 8 to 10 with Eriochrome Black T indicator. Alternatively standardize by titrating cupric nitrate (electrolytic copper metal as primary standard) by the procedure given below.

Naphthylazoxine. Prepare a 1% solution in dimethylformamide.

$0.005M$ Cupric Nitrate. Prepare an aqueous solution from reagent grade cupric nitrate.

PROCEDURE

Take a sample containing 0.15 to 0.40 mmole of the metal ion to be titrated and adjust the volume to 50 to 75 ml. If a masking agent is needed, add 5 to 10 ml. of $0.1M$ solution for each 0.1 mmole of ion to be masked. Consult Table I for information regarding the suggested buffer and pH to be used. Add the buffer and check the pH of the solution with a pH meter. If it is not in the correct range, adjust the pH further with dilute ammonia or perchloric acid. Add 0.5 ml. of naphthylazoxine indicator, and titrate with $0.05M$ EDTA until the indicator changes to its full red color. Add 1.00 ml. of $0.005M$ cupric nitrate and titrate to the sharpest color change from yellow or yellow-orange to red. Run a blank on each batch of $0.005M$ cupric nitrate and subtract this from the buret reading.

If cobalt, lead, or zinc is titrated and the pH is in the range from 6.0 to 6.5, the addition of $0.005M$ cupric nitrate may be eliminated. If this is done, take the end point as the point when the indicator attains its maximum red color.

TITRATIONS WITH COPPER(II) ADDED

When $0.05M$ EDTA is used with naphthylazoxine indicator, the titration for zinc gives a sharp end point from yellow to red between pH 5.5 and 6.5; copper is titrated sharply if the pH is in the approximate range from 3.5 to 6.5. Cobalt and lead also give fairly sharp end points in weak acid solution. Most other metals form only a weak azoxine complex and give a gradual color change in the vicinity of the stoichiometric point. In such cases the determination can usually be carried out successfully if a small, measured quantity of copper(II) is added near the end of the titration.

A specific example of this is the titration of lanthanum. Lanthanum reacts with naphthylazoxine but the complex formed is weak, so that the end point color change is gradual and begins too soon. This is illustrated on the theoretical curve for titration of lanthanum at pH 6 with EDTA (Figure 2). By adding a small amount of copper(II), which forms a rather strong complex with naphthylazoxine, a sharp color change occurs when the sum of copper (II) and lanthanum has been titrated. This is shown by the curve in Figure 2 in which pCu is plotted against milliliters of EDTA.

As copper(II) forms a stronger EDTA complex ($\log K = 18.8$) than lanthanum ($\log K = 15.5$), it might seem at first that the cupric azoxine complex would be broken by EDTA before all of the lanthanum is titrated. However, the

Table I. Suggested Conditions for Titration

Ion(s) Titrated	pH Range	Buffer
Cd^{++}, Co^{++}, Cu^{++}, Pb^{++}, Ni^{++}, rare earths, Y^{+++}, Zn^{++}	5.5 to 6.5	Ammonium acetate (~2g.) or pyridine (5 to 10 drops)
Cu^{++} (alone)	4.0	Formate
Mn^{++}	6.5 to 7.0	Pyridine (10 drops)
Fe^{+++}, Th^{+4}	3.0 to 3.5	Chloroacetate
Cd^{++}, Co^{++}, Cu^{++}, Pb^{++}, Ni^{++}, Zn^{++} in presence of citrate or tartrate	6.0 to 6.5	Ammonium acetate (~2g.) or pyridine (5 to 10 drops)

Table II. Titration of Metal Ions with 0.05*M* EDTA and Naphthylazoxine Indicator

Ion	Theoretical	Actual[a]	Difference	pH at End Point
Cd^{++}	9.87	9.85	−0.02	5.4
		9.85	−0.02	5.5
Co^{++}	9.14	9.14	0.00	5.0
		9.13[b]	−0.01	5.6
		9.13	−0.01	5.6
Cu^{++}	9.01	9.02	+0.01	3.6
		9.00	−0.01	3.6
		9.00	−0.01	3.6
La^{+++}	9.27	9.27	0.00	6.4
		9.24	−0.03	5.6
		9.28	+0.01	6.3
Ni^{++}	9.23	9.22	−0.01	5.2
		9.23	0.00	5.2
		9.25	+0.02	5.9
Th^{+4}	4.33	4.34	+0.01	3.2
		4.34	+0.01	3.2
		4.33	0.00	3.4
Y^{+++}	9.79	9.82	+0.03	5.4
		9.85	+0.06	5.4
		9.81	+0.02	5.2
Yb^{+++}	9.77	9.78	+0.01	5.2
		9.77	0.00	5.2
		9.77	0.00	5.2
Zn^{++}	9.11	0.09	−0.02	5.2
		9.08	−0.03	5.3
		9.10[b]	−0.01	6.1

[a] 1 ml. of 0.005*M* copper(II) added except where noted.
[b] No copper added.

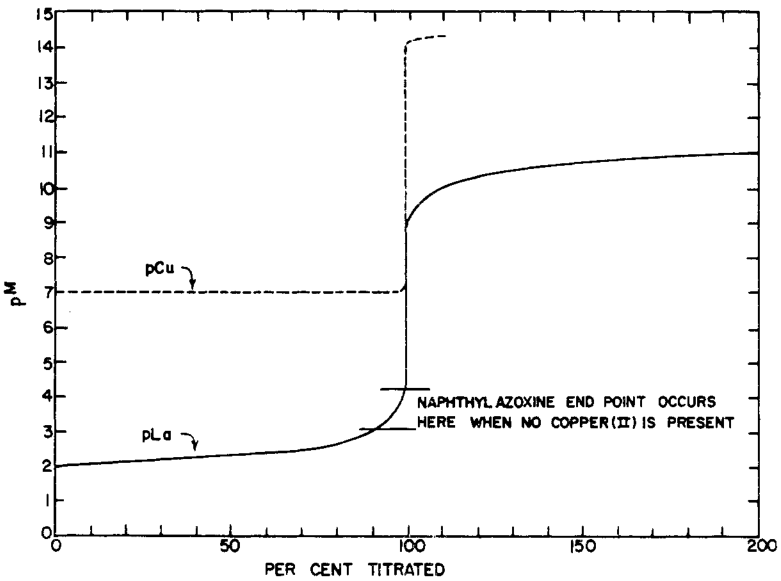

Figure 2. Theoretical curve for titration of lanthanum

driving force of a complex formation reaction can be estimated from the difference in formation constants of the complexes involved. The reaction of interest in the present case is the conversion of copper(II) azoxine (CuIn) to copper(II) EDTA.

$$\text{CuIn} + \text{EDTA} \rightleftharpoons \text{Cu EDTA} + \text{In} \quad (1)$$

Taking the formation constant reported for copper(II) 8-quinolinol-5-sulfonic acid (*4*) as an estimate of the constant for the related compound, naphthylazoxine, the constant for Reaction 1 may be approximated.

$$K = \frac{K_{\text{EDTA}}}{K_{\text{in}}} = \frac{10^{18.8}}{10^{11.5}} = 10^{7.3}$$

The reaction of lanthanum with EDTA may be considered to be merely

$$\text{La}^{+++} + \text{EDTA} \rightleftharpoons \text{La EDTA} \quad (2)$$

because the copper(II) forms a complex with naphthylazoxine sufficiently stable so that none of the indicator may be considered as being available to the lanthanum. The formation constant for Reaction 2 is, therefore, $10^{15.5}$ compared to $10^{7.3}$ for Reaction 1.

This is more qualitative than quantitative. An acid solution makes an important difference in the strength of all complexes and this was not taken into account. Also, incorporation of the hydrolysis constants for lanthanum in Reaction 2 would make some difference at the slightly acid pH of the titration.

TITRATION OF SINGLE METAL IONS

The following metals can be titrated directly with EDTA at pH 5.5 to 6.5 using naphthylazoxine indicator with copper(II) added: cadmium, cobalt, copper(II), lead, nickel, rare earths, yttrium, and zinc. At this pH aluminum, iron(III), thorium, and zirconium react irreversibly with the indicator. At pH 3.0 to 3.5, however, thorium and iron(III) can be titrated directly if a small amount of copper is added. The EDTA complexes of magnesium and the alkaline earths are too weak to be titrated in acid solution.

The precision and accuracy were studied by titrating portions of carefully standardized metal ion solutions (Table II). The solutions taken for analysis were standardized as follows: cadmium by EDTA titration using Eriochrome Black T indicator; cobalt by titration of the acid formed on passing the cobalt perchlorate solution through a hydrogen-form cation exchange column; copper, nickel, and zinc solutions by using the pure metal as a primary standard; thorium by EDTA titration using Alizarin Red S indicator (*2*); lanthanum by EDTA titration using Thorin indicator (*3*).

INTERFERENCE STUDY

Magnesium forms a rather weak complex with EDTA (log $K = 8.7$) and does not interfere in titrations where the pH is 6.0 or below. Calcium represents a near-borderline case (log K of EDTA complex = 10.7) but does not interfere provided the pH of the titration is not greater than 5.5. Manganese (II) (log K = 13.8) interferes in all titrations carried out at pH 5.5 to 6.5, but can be quantitatively titrated with other divalent metals if the pH is in the range from 6.5 to 7.0. All divalent metals forming EDTA complexes having a log K greater than about 13 interfere in the titration of thorium at pH

3.0 to 3.5. Copper may be quantitatively titrated together with thorium.

In titrations with azoxine indicators at pH 5.5 to 6.5, no end point can be obtained if macro amounts of aluminum, iron(III), thorium, or zirconium are present. However, as shown by the data in Table III, traces of these ions will not interfere with the end point. This is of practical significance, especially in EDTA titrations following separations, because it permits the use of separations that sometimes leave traces of the tri- or quadrivalent metals.

The effect of inorganic anions and organic chelating agents was studied by titrating zinc in the presence of an approximately equimolar concentration of the added ion or compound. These titrations were carried out at pH 6.4 ± 0.2 (acetate buffer) without added copper. The results, summarized in Table IV, indicate that, at least in this particular titration, a wide variety of chelating ions can be tolerated. It should also be mentioned that sulfate, acetate, chloroacetate, and the like do not interfere in the naphthylazoxine method for thorium, as is the case with the Alizarin Red and other indicator methods.

Table III. Cation Interference Study

Ion Titrated	Ion Added, 0.05M	Ml.	Ml. 0.05M EDTA Theoretical	Actual	Diff.	pH at End Point
Cd^{++}	Mg^{++}	6.0	5.12	5.13	+0.01	5.5
Cd^{++}	Ca^{++}	6.0	5.12	5.12	0.00	4.9
Cd^{++}	Ca^{++}	6.0	5.12	5.29	+0.27	5.6
Co^{++}	Mg^{++}	6.0	4.73	4.72	−0.01	5.6
Co^{++}	Ca^{++}	6.0	4.73	4.73	0.00	5.6
Mn^{++}	Mg^{++}	5.0	5.18	5.20	+0.02	5.8
Mn^{++}	Ca^{++}	5.0	5.18	fails	. . .	5.7
Ni^{++}	Mg^{++}	5.0	4.69	4.66	−0.03	5.7
Ni^{++}	Ca^{++}	5.0	4.69	fails	. . .	5.6
Zn^{++}	Mg^{++}	6.0	5.09	5.08	−0.01	5.6
Zn^{++}	Ca^{++}	6.0	5.09	5.10	+0.01	4.9
Zn^{++}	Al^{+++}	0.05	5.19	5.19	0.00	6.4
Zn^{++}	Fe^{+++}	0.05	5.19	5.19	0.00	6.4
Zn^{++}	Th^{+4}	0.05	5.19[a]	5.23	+0.04	6.4
Zn^{++}	Zr^{+4}	0.05	6.33	6.33	0.00	6.4

[a] Theoretical EDTA is 5.24 ml. if thorium is also titrated.

Table IV. Effect of Anions and Chelating Agents

Conditions: 5.00 ml. of 0.05360M zinc nitrate titrated with 0.0518M EDTA, pH 6.4 ± 0.2, naphthylazoxine indicator, no copper(II) added

Ion Added	Ratio of Ion Added to Zn	Dev. from Theory Ml. EDTA	Remarks
F^-	2 to 1	0.00	
Br^-	2 to 1	+0.02	
I^-	2 to 1	0.00	
SO_4^{--}	2 to 1	+0.01	
PO_4^{---}	2 to 1	0.00	Must titrate slowly
CN^-	2 to 1	0.00	End point orange but sharp
SCN^-	2 to 1	0.00	
Ascorbic acid	20 to 1	+0.01	
2.3-Dimercapto-1-propanol	5 to 1	. . .	Fails
Citric acid	20 to 1	0.00	Excellent
Ethylenediamine	2 to 1	0.00	
Iminodiacetic acid	2 to 1	0.00	Fair, long orange range
Malonic acid	2 to 1	0.00	Excellent
Oxalic acid	2 to 1	0.00	
Tartaric acid	20 to 1	0.00	

USE OF MASKING AGENTS

The selectivity of EDTA titrations using azoxine indicators can be greatly improved through the use of masking agents. One important example is the titration of metal ions in the presence of uranium(VI) using tartrate or citrate to complex the latter. If present in very high concentration, the yellow color of the uranyl complex prevents satisfactory visual observation of an end point, but it should still be possible to detect the end point photometrically.

Citrate will mask thorium and zirconium (but not aluminum or rare earths) and permit the titration of zinc and the like with EDTA. This is quite striking because the log K for zinc EDTA is 16.6 and for thorium EDTA is 23.2. It is also of important practical value. For example, a mixture of thorium and zinc can be analyzed by titrating the zinc with EDTA (naphthylazoxine indicator) using citrate to mask the thorium; the thorium is determined in the presence of zinc by an EDTA titration at pH 2.5 (Alizarin Red S indicator).

Several metals do not complex readily with EDTA, but will interfere unless they are kept in solution by means of a suitable complexing agent. Antimony is taken care of by the addition of tartrate, and interference by beryllium niobium, and tantalum is prevented by the addition of fluoride.

Table V. Titrations Using Masking Agents

Conditions: Ratio of ion masked to ion titrated, 1 to 1. Titration with 0.05M EDTA, naphthylazoxine indicator, no copper(II) added

Ion Titrated	Ion Masked	Masking Agent	pH at End Point	Ml. EDTA Theoretical	Actual	Diff.
Cd^{++}	UO_2^{++}	Tartrate	5.6	9.86	9.85	−0.01
Co^{++}	UO_2^{++}	Tartrate	5.8	9.14	9.17	+0.03
Ni^{++}	UO_2^{++}	Tartrate	5.9	9.23	9.24	+0.01
Yb^{+++}	UO_2^{++}	Tartrate	5.3	9.10	9.12	+0.02
Zn^{++}	Ag^+	Chloride	6.4	5.19	5.19	0.00
Zn^{++}	Al^{+++}	Citrate	6.4	5.19	fails	. . . .
Zn^{++}	Be^{++}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Cu^{++}	Thiourea	6.4	5.19	5.19	0.00
Zn^{++}	Hg^{++}	Iodide	6.4	5.19	5.20	+0.01
Zn^{++}	Nb^{+5}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Sb^{+++}	Tartrate	6.4	5.19	5.19	0.00
Zn^{++}	Sn^{++}	Citrate	6.4	5.19	5.19	0.00
Zn^{++}	Sn^{+4}	Citrate	6.4	5.19	fails	. . .
Zn^{++}	Ti^{+4}	Fluoride	6.4	5.19	5.19	0.00
Zn^{++}	Th^{+4}	Citrate	6.4	5.19	5.19	0.00
Zn^{++}	UO_2^{++}	Tartrate	6.0	9.10	9.12	+0.02
Zn^{++}	Zr^{+4}	Citrate	6.4	5.19	5.19	0.00

Several other masking possibilities have been demonstrated. Zinc can be titrated in the presence of copper by adding thiourea to complex the latter. Iodide serves as an almost specific masking agent for mercury(II). Copper can be titrated at pH 3.0 to 3.5 without interference from aluminum if fluoride is added. This titration fails at higher pH values. Data for these and other titrations using masking agents are presented in Table V.

DISCUSSION

In order to obtain rapid equilibrium near the end point in titrations where some copper must be present, the copper should be added near the end point. The titration of thorium is an exception; here the equilibrium is rapid even when the copper is added at the start of the titration. In titrations where a masking agent such as citrate is present, it is advisable to delay adding the naphthylazoxine indicator until a few tenths of a milliliter before the expected end point.

When determining metals that form weak azoxine complexes (rare earths, for example), zinc can be added instead of copper in order to obtain a sharp end point. Zinc gives better results than copper for titrations to be carried out in the presence of calcium, but the addition of copper affords a greater toleration for chelating agents.

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Determination of Monomeric Epsilon-Caprolactam and Moisture in 6 Nylon

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▶ A rapid procedure for the simultaneous determination of ε-caprolactam monomer and moisture in 6 nylon flake and yarn is described. They are separated from the sample by vacuum extraction at 200° C., the monomer and part of the moisture being condensed in a water-ice cold trap. The monomer is determined by refractive index in an aqueous dilution of the condensate, while moisture is obtained by difference. The procedure requires less than 3 hours as compared to the 24-hour water-extraction procedure for the determination of total water-extractable material and, when used in conjunction with the water-extraction procedure, it furnishes an estimate of the dimer content plus any low molecular weight, water-soluble, linear molecules present in the polymer.

In the polymerization of ε-caprolactam (hereafter referred to as monomer) to 6 nylon (a polycaproamide produced by polymerization of ε-caprolactam), it is important to be able to determine the amount of unpolymerized lactam remaining in the polymer. Hanford and Joyce (*1*) employ a 30-minute vacuum extraction at 180° C. to determine monomer in the polymer. The monomer is condensed on a dry ice–acetone cold finger, dissolved in acetone, recovered by evaporation of the acetone, and finally dried and weighed. Van Velden and coworkers (*3*) have determined, separately, monomer, ring compounds, and short linear molecules in 6 nylon. Hot methanolic extraction up to 36 hours is followed by evaporation and careful drying. Monomer is determined by sublimation and weighing. The ring compounds and short linear molecules left after sublimation of the monomer are separated by a strongly basic ion exchange resin.

The amount of water-soluble material in 6 nylon can be determined by Soxhlet extraction for 16 hours in the case of $^1/_8$-inch flake or 8 hours in the case of yarn. This procedure is based on the loss in weight of the sample and involves careful drying of Soxhlet thimbles and of the extracted sample. An independent sample moisture analysis is required to allow results to be expressed on a dry sample basis. These steps are subject to considerable error and require about 24 hours. Furthermore, an estimate of monomer plus dimer (dimer, as used in this paper, is a mixture of cyclic dimer, trimer, etc.) and water-soluble linear molecules is obtained, whereas results for monomer alone are often desirable.

This paper presents a vacuum extraction technique which is rapid, accurate, and specific for monomer in the presence of 6 nylon, dimer, and moisture. The extraction is carried out at 200° C., and the monomer is condensed in a cold trap, dissolved in water, and determined by refractive index measurement. Since the total sample weight loss represents monomer plus moisture, the latter is obtained by difference.

APPARATUS

The glassware is constructed of Pyrex chemical glass No. 7740 and is illustrated in a schematic assembly in Figure 1. The sample tube is 180 mm. long overall and 25 mm. in outside diameter with a 35/25 socket joint. The glass bridge is constructed of tubing 20 mm. in outside diameter with 35/20 and 28/15 ball joints. The trap is 32 mm. in outside diameter and 255 mm. long over-all; outside diameters for the central tube, the side arm, and the nipple are 20, 11, and 15 mm., respectively, and the socket joints are 28/15 and 18/9. The bottom end of the central tube of the cold trap is displaced toward one wall to allow easier entry of water into the tube when dissolving the monomer and when shaking and mixing the solution. The No. 28 and No. 35

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