CHEMICAL METHODS OF ANALYSIS

THE POLAROGRAPHIC ANALYSIS OF ORGANIC COMPOUNDS BY INDIRECT METHODS (Review)

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Translated from Zavodskaya Laboratoriya, Vol. 28, No. 1,
pp. 5-11, January, 1962

Many organic compounds are inactive polarographically, and, in order to determine them, it is necessary to carry out some preliminary reactions to convert them to polarographically active substances [1].

In addition to their analytical value, the use of these reactions in polarography often leads to the obtaining of valuable data on the kinetics and equilibria of the reactions themselves. No reviews have been published specially devoted to this field of polarography, and only in one article [1] could we find any systematic account of the literature (up to 1953) on this subject.

In the present paper we have considered articles dealing with the polarographic analysis of organic compounds by means of indirect reactions*.

Reactions with Metal Ions

Complex formation with metal cations has been used for the indirect polarographic determination of amino acids. Preliminary separation of copper and nickel complexes, by paper chromatography [2-7] or by electrophoresis [8], has been used for this purpose. Freshly prepared $Cu(OH)_2$ reacts with α-amino acids (1 mole of Cu^{2+} with 2 moles of amino acid). The dissolved complex can be determined polarographically at a controlled pH [3]. However, according to [9], the proportionality between diffusion current and amino acid concentration is disturbed in the presence of a $Cu(OH)_2$ deposit. Removal of the precipitate by centrifuging does not improve the results. One author [9] recommends amperometric titration of the amino acid solution with Cu^{2+} in aqueous dimethylformamide, in the presence of salicylaldehyde as indicator.

Satisfactory results are obtained with copper phosphate at pH 8.75-8.90, with subsequent centrifuging to remove unreacted phosphate [10].

Oscillographic polarography has also been used for determining copper complexes of amino acids [11]. The corresponding copper complex has been used for the polarographic analysis of nitrilotriacetic acid [12].

Amino acids (N, N-ethylenediglycine) and nitrilotriacetic acid have also been determined by means of $Cd(OH)_2$, which is converted into a soluble cadmium complex at pH 10 [13, 14]. The anodic wave of its cobalt complex has been used for determining histidine [15].

Ethylenediaminotetraacetic acid and 1, 2-diaminocyclohexane-N, N, N, N-tetraacetic acid form mercury complexes, so that these organic compounds give anodic waves at a dropping mercury electrode [16]; ethylenediamine behaves similarly [17].

Acetylene forms a mercury acetylide and can therefore be determined by oscillographic polarography [18]. Nickel gives a soluble complex with 1,2-diaminocyclohexane (reaction with precipitated $Ni(OH)_2$ at pH 11.7), so that the content of the latter in hexamethylenediamine can be measured polarographically [19].

A number of organic compounds can be determined by reaction with a metal ion to form a precipitate, separation of the latter, followed by dissolution and polarographic estimation of the metal. For instance, carazole (1,5-pentaethylene-1,2,3,4-tetrazole) reacts with copper ions to give a precipitate; this is dissolved in a mixture of NH_3, NH_4Cl, and Na_2SO_3, and the copper is determined polarographically [20]. In another paper [21], volatile amines (methylamine and ethylamine) are precipitated by reaction with Nessler's solution. The precipitate is separated and dissolved in sodium thiosulfate solution, and the mercury thiosulfate complex is estimated polarographically.

A convenient method is to polarograph the metal solution after reaction with the organic compound, and to deduce the concentration of the latter from the reduction in wave height. This has been applied to the polarographic analysis of antimalarial preparations (reaction with HgI_4^{2-}) [22] and of propylenediamine (reaction with copper ions) [23].

* Methods based on the suppression of polarographic maxima are not considered here.

The polarographic determination of thiamine is based on precipitate formation with potassium bismuth iodide. The precipitate is separated and dissolved in sodium potassium tartrate, and the anodic wave of the iodide ion is recorded [24].

The Nitration Reaction

Nitration is the most frequently used reaction for the determination of benzene and its homologs. The nitration is carried out [25] with a mixture of equal volumes of concentrated nitric and sulfuric acids. Benzene is converted to dinitrobenzene, which is polarographed, after neutralization, in a concentrated alkali medium. This method has been used, in particular, for determining benzene in expired air [26].

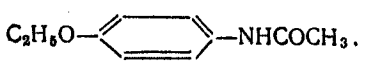
In order to determine benzene in the presence of toluene and xylene [27], the mixture is nitrated at 100° for 15 min, and the nitrocompounds are then extracted with ether. The ether is evaporated off, and the dinitrotoluene and dinitroxylenes are oxidized by chromic acid to the corresponding nitro acids; these acids are then converted into salts, and the dinitrobenzene is separated from them by ether extraction.

According to [28], toluene can be separated from benzene in air by passing the latter through chromic mixture. Nitration, with and without preliminary passage of the air through chromic mixture, gives two samples of nitrocompounds, and the difference in wave heights can be used to calculate the toluene content of the air.

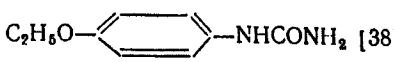
The method [27] of determining benzene in the presence of its homologs has been improved [29] by selective extraction of the dinitrobenzene with pyridine from the nitration mixture (10 g NH_4NO_3 in 100 ml H_2SO_4; nitration for 5-10 min), after oxidation with CrO_3, so as to remove the need for two extractions with ether. Polarography in pyridine eliminates the formation of a dinitrobenzene precipitate.

A disadvantage of this method is that the calibration curve is not a straight line.

The nitration reaction has also been applied to the determination of triortho-cresyl phosphate $(CH_3C_6H_4O)_3PO_4$ and benzene [30], phenol [31], toluene [32], para-cresol [33] (in all cases the corresponding dinitro compound was obtained) naphthalene [34] and para-toluic acid [35]. Nitration has been used for determining [36] propamine, methylpropamine, morphine [37], acetophenetidine



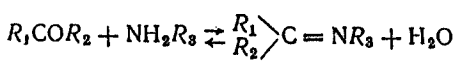
dulcine


[38]

and tyrosine [39].

The Reaction of Formation of a Schiff's Base (Imino Group)

Carbonyl compounds react with primary amines to form a so-called Schiff's base:



These bases are polarographically active and can be reduced at a dropping mercury electrode at a more positive potential than that for the corresponding carbonyl compounds. This makes it possible to determine carbonyl compounds which have a high negative reduction potential and polarographically inactive amino acids.

It has been found [40-46] that, for determining carbonyl compounds – cyclopentanone [40], extrone [42], 17-ketosteroids [40, 43, 44], camphors [46] – it is convenient, before polarography, to convert them into Schiff's bases using the Zhirara reagent $(CH_3)_2NCH_2CONHNH_2$ [40, 42, 44-46], the monohydrazide of maleic acid, or aminoguanidine [43]. Hydrazine and phenyl hydrazine have been used with acetone, methyl isobutyl ketone, and methyl n-amyl ketone, to obtain the corresponding Schiff's bases [41]. Further improvements in the method for determining acetone are to condense it to a Schiff's base with ammonia or glycine [47, 48], semicarbazide [49], n-butylamine [50], hexamethylenediamine or ethylenediamine [51]. In all cases rapid equilibrium is obtained for formation of the imino derivative, and the diffusion current is proportional to the acetone concentration.

Several papers have been devoted to a polarographic study of the kinetics and equilibria of the reactions between carbonyl compounds and primary amines. Descriptions have appeared of the reactions of pyruvic acid with histamine and histidine [52], ammonia [53], glycine, alanine, and colamine [54], of the oxidation product of ascorbic

acid with ammonia [55], of acetone with ammonia and glycine [48], and of cyclopentanone, cyclohexanone, and methylcyclohexanone with ammonia, methylamine, ethanolamine, ethylamine, glycine, and alanine [56]. In all cases the group $\rangle C{=}N-$ reduced at a more positive potential than did the $\rangle C{=}O$ group, and one molecule of carbonyl compound reacted with one molecule of amine. In calculating the equilibrium, account was taken of the interaction:

$$\rangle C = NR + H^+ \rightleftarrows \rangle C = NRH^+.$$

The electrode reaction is between the protonized form of the imino compound and two electrons [56, 57]:

$$\rangle C(H^+) = NR + 2e + 2H^+ \rightarrow \rangle CH(H^+)NHR.$$

It is recommended that methylamine should be used for determining cyclopentanone, cyclohexanone, and methylcyclohexanone [56]. Hexamethylenediamine or ethylenediamine are used in [51] for this purpose and for the analysis of aldehydes. Glycine is to be preferred to ammonia for determining acetone, since it gives a higher wave [48].

A polarographic study has been carried out of the interaction products of benzaldehyde with hydrazine, 1,1-dimethylhydrazine, and monomethylhydrazine [58]; clear waves were observed at pH about 11.

Reaction with hydrazine (pH 2.3) has also been used for determining aldopentoses [59]. The reaction of semicarbazide with carbonyl compounds has been employed for determining acetone, methylisobutyl ketone, acetaldehyde, cyclohexanone, butyric aldehyde, crotanaldehyde, and acrolein, in the form of the corresponding semicarbazones [49]. The half-wave potentials of these semicarbazones are in the range −1.0 to 1.3 v (S.C.E.).

A detailed study has been made [60] of the polarographic behavior of the interaction products of pyrrole-2-aldehyde with various amines. The formation and precipitation of Schiff's bases have been described; the aldehyde content can be determined from the excess of 2, 4-dinitrophenylhydrazine [61]. The same principle has been used for amperometric titration of carbonyl compounds [62].

Amino acids (glycine, alanine, and colamine) can be analyzed polarographically by means of the reaction with pyruvic acid or acetone [48, 54]. Use of reduction in the wave height of phthalic aldehyde has also been proposed as a means of determining amino acids [63].

The reaction with isobutyric aldehyde has been employed for the estimation of primary amines [64]. Ammonia and secondary and tertiary amines do not interfere; the half-wave potential for the corresponding Schiff's bases is −1.5 v, while that for isobutyric acid is −2.1 v.

Reaction with formaldehyde has been used for the polarographic determination of ε-aminocaproic acid, the corresponding caprolactam after hydrolysis to ε-aminocaproic acid, and aminoenanthic, aminopelargic, and aminoundecanoic acids [65, 66]. Two variants of this method have been developed: In the first variant [65], the reaction with formaldehyde is carried out in an alkaline medium (0.1 M), where the yield of Schiff's base or methyl derivative is a maximum. Polarography is then carried out in 0.1 M acid, which gives better conditions for the electrode reaction. In the second variant [66], both the reaction and the polarography are carried out in the same buffer solution at a pH which gives the maximum limiting current (for the analysis of ε-aminocaproic acid and caprolactam the pH is 8.0-8.2, and the supporting electrolyte is 0.5 M $NaHCO_3$). The formaldehyde concentration should be constant (1.5-3.0%).

The Nitrosation Reaction

Secondary aliphatic amines, and secondary and tertiary aromatic and alkylaromatic amines, are polarographically inactive, but can be determined after conversion to the corresponding nitroso compounds. The method is suitable for qualitative identification of secondary aliphatic amines in the presence of primary and tertiary aliphatic amines.

A method has been developed [67] for determining dimethylamine in the presence of ammonia, monomethylamine, and trimethylamine in oils. Other authors [68-71] have described the estimation of dimethylamine and neostygmine in a similar way.

Nitrosation has also been used for the determination of diphenylamine [72-74], N-ethylaniline [72], piperidine [74], dicain (the chloride of the dimethylaminoethyl ester of n-butylaminobenzoic acid) [75], antipyrine and its salts [76], N-allylnormorphine [77], products of the benzidine transformation [78], rutine (a γ-pyrone derivative) [79], proline and hydroxyproline (pyrrole derivatives) [80].

The Halogenation Reaction

This method has been most widely used for the polarographic determination of unsaturated organic compounds with isolated double or single bonds. Iodination has been employed for the indirect polarographic estimation of β-carotene [81-83]. Halogenation has also been used for determining a number of monoolefins [84]. A method has been proposed for estimating ethylene and vinyl chloride following their bromination to dibromoethane and chloro-1,2-dibromoethane [85]. Excess of bromine is removed with ammonia. Bromination has also been used for determining gaseous unsaturated compounds—ethylene, propene, n-butene, vinyl chloride—and liquid unsaturated compounds—allyl alcohol, dichloroethylene, methyl methacrylate, methacrylic acid, butyl acrylate, butyl methacrylate [86]. The brominating agent is a 3 M solution of Br_2 in methyl alcohol, saturated with sodium bromide. The corresponding dibromo derivatives are formed in all cases. In the analysis of a mixture of methyl methacrylate and methacrylic acid [87], the latter is determined before bromination, and then the total amount of the two after bromination to the corresponding dibromo derivatives.

It has been proposed [88] to carry out bromination (5 M Br_2 in glacial acetic acid for 24 hr) for the polarographic determination of acetylene, vinyl chloride, 1,2-dichloroethylene, and 1,1,2-trichloroethylene. This has proved successful for the analysis of mixtures of acetylene with 1,1,2-trichloroethylene and of vinyl chloride with 1,2-dichloroethylene.

Bromination has also been used for determining but-2-yne-1, 4-diol in mixtures with but-2-enediol, but-2-anediol [89], caffeine, theobromine, and theofelline [90].

Vitamin A can be determined, after iodination, from the size of the anodic wave [91].

The Oxidation Reaction

The oxidation reaction is often used for the indirect determination of a compound containing an alcoholic group, which is oxidized to the corresponding carbonyl group. Analytical methods have been developed, based either on the consumption of oxidant or on the amount of carbonyl compound formed.

Determinations have been carried out in which 17-hydroxysteroids are oxidized by aluminum tertbutylate to 17-ketosteroids [92, 93]; acetoin (dimethylketol) is oxidized by ferric chloride to diacetyl [94]; d-serin [95] and ethane- and propane-1, 2-diols [96] are oxidized by periodic acid; glycerol is oxidized to formic acid by periodic acid [97]; lactic acid is oxidized to acetaldehyde by potassium permanganate [98].

Diethylene glycol and dipropene glycol can be determined in mixtures with monoglycols by oxidizing the latter with periodic acid and distilling. The diglycols are then oxidized with potassium bichromate and determined polarographically from the amount of bichromate consumed [99]. Other glycols [100-102], mannitol, sorbitol [103], and blood sugar [104] can be determined from the excess of periodic acid or its salts remaining after oxidation [100, 101, 103, 104], and from the amount of aldehyde formed [102].

It has been proposed to determine ethyl alcohol in blood by oxidation with potassium bichromate, followed by polarographic estimation of the excess oxidant [105-107], or of the reaction product, acetaldehyde [108].

Alcohols (isopropyl and others) can be determined by oxidation with chromic acid, followed by polarography of the excess oxidant. The cis- and trans- forms of 2-methylcyclohexanol oxidize at different rates, so that they can be determined separately [109, 110].

It has been proposed to determine the vapors of methyl and ethyl alcohols separately in a mixture by passing the mixture through lead chromate granules at 600° [111]. The formaldehyde and acetaldehyde produced can be determined separately by polarographic means.

The following oxidants have also been used: periodate for determining adrenalin and noradrenalin [112], permanganate for mandelic acid [113], an oxidizing mixture of KBr + $KMnO_4$ + H_2O_2 for citric acid [114], nitric acid for narcotine and hydrastine [115].

Methionite has been determined by oxidation with PbO_2 and subsequent estimation of Pb^{2+} [116].

The Hydrolysis Reaction

Hydrolysis has been applied to the polarographic determination of polarographically inactive pentoses and pentosans in cellulose [117-119], lignin [120, 121], cellulose [122], maleic anhydride (hydrolysis to maleic acid) [123], diacetylmorphine (hydrolysis and conversion to nitrosomorphine) [124], antimalarial preparations [125], vinyl acetate, butyrate, and benzoate [126], and para-nitrophenylhydrazones of polyvinyl alcohols (hydrolysis to hydrazines) [127].

It has been proposed to determine melathione (1,2-dicarboethoxyethyl-O, O-dimethyldithiophosphate) by hydrolyzing it in alkaline solution to fumaric acid [128].

Saccharose and raffinose can be determined polarographically after hydrolysis by acid to the polarographically active fructose. Glucose does not interfere [129].

Starch can be hydrolyzed by acid to the polarographically active 5-hydroxymethylfurfural [130].

It has been proposed to determine norcotolin by hydrolysis in a weakly alkaline medium to catornolin (a derivative of o-hydroxybenzoic aldehyde) [131].

Other Reactions

Diazotization has been proposed for determining primary aromatic amines [132-134]. Acetone, methyl ethyl ketone, cyclopentanone, and other ketones can be determined from the decrease in the SO_2 wave added to sodium sulfite in an acid medium [135, 136]. Free carbonyl groups in quinones can be determined by the same method [137].

Mercapto groups in proteins can be determined by means of the reaction with sodium para-chloromercuribenzoate [138-140]. Histamine and histidine can be determined by means of the reaction with carbon disulfide to form the polarographically active β-imidazolyl-α-dithiocarbaminopropionic and β-imidazolylethyl-α-dithiocarbamic acids respectively [141]. The purity of amino acids can be determined in the same way [142].

The polarographically inactive anions of the aci-forms of nitro compounds, containing primary or secondary nitro groups (nitromethane, nitroethane, nitrocyclohexane in alkaline solution), have been determined by Ya. I. Tur'yan and V. V. Smekalova by means of the reaction with formaldehyde to give the corresponding polarographically active nitroalcohols. The same authors have used the reaction with formaldehyde for determining cyclohexanone oxime and hydroxylamine. This avoids the disturbing effect of hydrolysis of cyclohexanone oxime, which is observed with direct polarography. It also becomes possible to estimate hydroxylamine polarographically in a strongly acid medium.

For the polarography of indene, use has been made [143] of its reaction with benzaldehyde to give a compound with conjugated double bonds; this reduces at a more positive potential than does indene.

In order to identify plastics, these have been subjected to dry distillation, followed by bromination and nitration of the distillation products [144]. Reference to a few other papers on the use of indirect polarographic methods in polymer chemistry, not included in this review, may be found in [145].

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A POTENTIOMETRIC METHOD FOR ANALYZING MIXTURES OF ORGANIC ACIDS WITH NITRIC ACID IN NONAQUEOUS MEDIA

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Translated from Zavodskaya Laboratoriya, Vol. 28, No. 1, pp. 11-13, January, 1962

The method is based on the titration of a mixture of nitric and organic acids, in methyl ethyl ketone with 0.1 N tetraethylammonium hydroxide in benzene-methanol, or in acetone with 0.1 N sodium hydroxide in aqueous acetone. It is used for analyzing production mixtures of nitric and α-hydroxyisobutyric acids.

In this paper we describe methods and present results for the analysis of mixtures of nitric acid with nitrobenzoic acids, mono- and di-nitrophenols, and α-hydroxyisobutyric acid. The analysis of mixtures of nitric and α-hydroxyisobutyric acids is particularly important in a new process for methacrylic acid synthesis for the production of synthetic rubber. Our investigations have shown that this analysis can be rapid and accurate, and can also be carried out in nonaqueous solvents.

The solvents used were methyl ethyl ketone and acetone, which showed adequate differentiating properties. The titrant solution was 0.1 N tetraethylammonium hydroxide in benzene-methanol, prepared as previously