on the measurement of a minimum of 200 particles. The procedure is facilitated if the number of particles per field under observation is limited to approximately 50 to 100. Lesser numbers require the examination of a proportionally larger number of fields, and greater concentrations may cause overlapping of the particles and the involuntary selection for measurement of the larger particles. Photomicrographs of dust deposits of optimum concentration for measurement show a satisfactory degree of dispersion using the hemacytometer–electrostatic precipitator method.

Many observers have ascertained that the median size of nonindustrial dust is approximately 0.5 micron and can be expected to range in size from 0.3 to 0.7 micron. The Owens jet dust counter has been satisfactorily used for the measurement and counting of particles within this size range. Table I indicates clearly that the hemacytometer method may be used satisfactorily for the collection of nonindustrial dust of submicron size and that size measurements on this type of dust agree with those obtained using the Owens jet apparatus.

The dust particles generated by such industrial processes as crushing, grinding, and screening are of greater size than those associated with the natural or nonindustrial environment. The size distribution of industrial dust in general has been reported (*2*), using other means of collection, to be 15.87% less than 0.8 micron, 50% (median) less than 1.4 microns, and 84.13% less than 2.5 microns. Table II shows the particle size distribution of industrial dust and mist encountered in the sodium bichromate manufacturing plant studied. The results agree closely with those to be expected of an industrial dust when collected by conventional methods. Furthermore, within the plant, samples collected in proximity to dust-producing processes, such as those carried on in the ore preparation department, had a median size (2.2 microns) greater than those in the maintenance building (1.1 microns) which is more remote from the major sources of dust pollution. This gradation is logical.

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RECEIVED March 13, 1950. This project was supported by a cancer control grant from the National Cancer Institute, U. S. Public Health Service, CS-887, Thomas F. Mancuso, M.D., project director.

Coulometric Titration of 8-Quinolinol

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A microtitration of 8-quinolinol with electrolytically generated bromine is described. The use of an improved electrometric indicator circuit permits direct titration of samples containing 0.4 to 2.0 mg. of 8-quinolinol with a precision of ±0.5%, in spite of the slowness of bromination. The amount of bromine used is measured by determining the number of coulombs of electricity passed through the electrolysis cell by electrolyzing at constant current and measuring the time. A simple, electronically controlled constant current source suitable for use in the titration is described.

THE estimation of 8-quinolinol (8-hydroxyquinoline, oxine) is important in the determination of metals that form insoluble precipitates with it. In the volumetric method, the metal quinolate precipitate is purified by a suitable procedure and the 8-quinolinol content is determined by dissolving in acid, adding an excess of brominating agent, and back-titrating with arsenite or thiosulfate. A direct titration with electrolytically generated bromine was studied and found to be practical. In this method, the amount of bromine generated is measured by determining the number of coulombs passed through the cell.

The use of electrolytically generated bromine in analysis is well established. It has been used for the determination of arsenite (*2*), thioglycols (*3*), mustard gas (*4*), thiocyanate, hydrazine, and hydroxylamine (*5*). It is especially useful for microtitrations, as the amount of bromine added is easily controlled and accurately measured for rates as low as 10^{-8} equivalent per second. No standard solutions are required and the method lends itself to routine use.

The principal reactions occurring in the analysis are those of bromine formation and bromination of oxine.

Formation of Br_2 at electrode.

$$2Br^- \longrightarrow Br_2 + 2e^-$$

Concurrently H_2 is formed at cathode.

$$2H^+ + 2e^- \longrightarrow H_2$$

Bromination of 8-quinolinol.

$$C_9H_7ON + 2Br_2 \longrightarrow C_9H_5ONBr_2 + 2HBr$$

The bromination of one mole of 8-quinolinol thus requires the passage of 4 faradays of electricity.

APPARATUS

Constant Current Source. The circuit of the constant current source used in these experiments is shown in Figure 1.

The output current flows through resistors *R*-1 and *R*-2, which are the input of a conventional voltage regulator circuit. The voltage regulator circuit holds the *IR* drop across *R*-1 and *R*-2 constant and compensates for changes in the output current.

This current can be varied between 0.5 and 20.0 ma. at will by adjustment of *R*-2. The rough value of the output current is read on the meter; more accurate values of the current are obtained by measuring the *IR* drop across *R*-7 with a potentiometer.

Resistances *R*-3, *R*-4, *R*-5, and *R*-6 are provided to maintain constant sensitivity in the voltage regulator circuit, and act to prevent the screen potential of the 6SJ7 tube from being greater than the plate potential, which is a condition of instability. The resistor used depends on the current drawn: *R*-3 is used for 0.5 to 1 ma., *R*-4 for 1 to 5 ma., *R*-5 for 5 to 11 ma., and *R*-6 for 11 to 20 ma. The ranges overlap considerably and the above values are given as a guide rather than as definite conditions.

The calibration resistor, *R*-7, is very important and its value should be accurately known. It may be omitted from the circuit, and an external resistor, such as a resistance box of proper current rating, substituted for it. In these experiments, *R*-7 was a specially wound resistor.

The output or calibration terminals may be short-circuited without damage to the current supply. The output circuit should not be opened while current is flowing, because the voltage at the break rises to the plate voltage value (approximately 300 volts), which can cause an unpleasant shock.

Severe line voltage fluctuations cause a change in the output current due to changes in the heaters of the tubes; this can be overcome by use of a constant voltage transformer ahead of the 110-volt input. With a constant voltage transformer, the maximum drift of the current from a center value is less than 1% over several hours and the average deviation is less than 0.1% for periods of half an hour. Load changes of up to 3000 ohms in the output circuit give less than 0.1% change in output current.

The standard for current measurement during this work was an Epply Laboratories, low temperature coefficient standard Weston cell, checked by comparison with several other Bureau of Standards calibrated standard cells used in conjunction with a Type K-2 potentiometer. A potentiometer of this quality is not necessary for routine work; student potentiometers are satisfactory. The potential of the standard cell did not change during this work within the limits of experimental error.

Coulometer System. The coulombs of electricity used in the titration are determined by measuring the time of electrolysis at constant current (cf. *2*). This time is measured by an electric stopwatch wired to the constant current supply, so that operation of *S*-1 (Figure 1) starts and stops the clock in unison with the output current. This stopwatch was a Model S-10, calibrated to 0.1 second, of the Standard Electric Time Company. Line frequency variations affect the timer, although this factor is usually negligible. This should be checked, however, during periods of power shortages; one set of incorrect results in this laboratory was found to be due to this cause and occurred during a regional power shortage.

Indicator System. The operation of the indicator system is as follows: Referring to Figure 2, *Ra* is adjusted so that approximately 25 microamperes pass through the meter, *M*. Because the resistance of the meter branch of the parallel circuit is matched with the resistance of the electrode branch, a current of about 25 microamperes passes through the electrodes. The detector electrode acquires a high resistance due to polarization, probably because of a film of hydrogen on the surface. Free bromine acts as a depolarizer, and when present, lowers the resistance of the electrode which permits the current through the electrodes to increase while that through the meter decreases. The end point is marked by a large, sudden drop of current in the meter circuit.

The indicator system used is a hybrid of the amperometric indicator of Myers and Swift (*2*) and the dead-stop indicator of Foulk and Bawden (*1*). The detection electrode (cathode) is a sheet of bright platinum 2.5 × 3.1 cm. (1 × 1.25 inches); phenomena which make this electrode an indicator for bromine are described by Myers and Swift. The system is very sensitive to free halogens, is stable, and does not require the special precautions of the indicator system of Myers and Swift.

The reference electrode (anode) of platinum used by Myers and Swift seemed to be erratic in early work on the system, and in this study was replaced by a large-capacity calomel half-cell. Later work has shown that the erratic behavior of the electrode was due to the hydrogen evolved by the electrolysis cathode, and that the platinum anode of Myers and Swift is suitable for this titration.

Titration Assembly. The schematic diagram of the titration assembly is given in Figure 3.

The electrolysis electrodes and the indicator cathode are platinum; the indicator anode is a low-resistance calomel half-cell. The electrolysis cathode is separated from the titration vessel by a low-resistance salt bridge and is immersed in dilute sulfuric acid. Dimensions of the electrolysis electrodes are not critical; dimensions of the indicator cathode affect the sensitivity (cf. *2*). The calomel cell and salt bridge must have a low resistance; commercial calomel cells used in pH work are not suitable because of the high resistance in the fiber capillary. The calomel cell and salt bridge may be replaced by a platinum anode.

The titration vessel is a tall-form electrolytic beaker with a rubber stopper to hold the electrodes and bridges. The solution is stirred at approximately 200 r.p.m. The stirrer speed is not as critical as the turbulent mixing it creates, which must be fast enough to prevent electrolyte with a relatively high concentration of bromine from reaching the indicator electrode until the end point is reached.

PROCEDURE

Preparation of Electrolyte and Sample. Prepare a 0.2 *M* sodium bromide solution from sodium bromide and water, free from oxidizing or reducing impurities. Add 50 ml. of this solution to the titration vessel to serve as the electrolyte.

Dissolve the metal quinolate in concentrated hydrochloric acid, avoiding a large excess of acid. Dilute in a volumetric flask to an

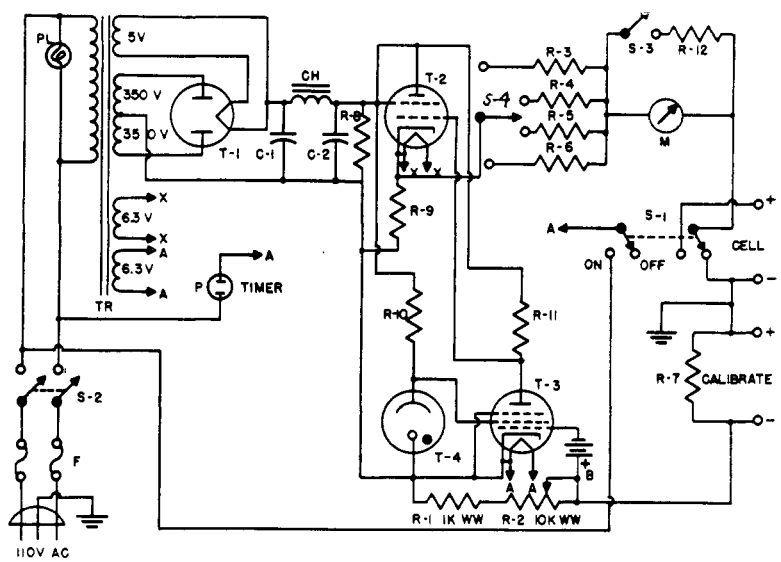

Figure 1. Constant Current Source

B. Battery, Burgess XX15E
C-1, *C*-2. Condenser, 20-microfarad, 450-volt, dry electrolytic
Ch. Choke, 30-henry, 80-ma., 350-ohm, Stancor C-1420
F. Fuse, 1-ampere, Littlefuse fusepost 1075-S, fuse 312001
M. Meter, 0–10 ma. scale, Simpson model 22S
P. Plug, chassis, female, Amphenol
PL. Pilot light, neon pilot light assembly, Dialco 91408
R-1. 1000-ohm, wire-wound, 10-watt
R-2. 10,000-ohm potentiometer, General Radio Company 371A
R-3. 4900-ohm, 1-watt
R-4. 15,000-ohm, 1-watt
R-5. 50,000-ohm, 1-watt
R-6. 150,000-ohm, 1-watt
R-7. Special resistor 5.000 ~ ± 0.003 ohm
R-8. 100,000-ohm, 2-watt
R-9. 100,000-ohm, 2-watt
R-10. 15,000-ohm, 10-watt
R-11. 500,000-ohm, 1-watt
R-12. Special resistor 0.789-ohm (50-ma. shunt for meter)
S-1. D.P.D.T. toggle switch
S-2. D.P.S.T. toggle switch
S-3. S.P.S.T. toggle switch
S-4. 4-way wafer switch, Centralab 2503
Tr. Transformer, Thordarson T 17R37
T-1. 5Y3GT or equivalent
T-2. 6L6
T-3. 6SJ7
T-4. 3/VR-90
Terminal posts for calibration and output were General Radio Company 138-V
Cabinet, 10 × 10 × 8 inches BUD, CU-880
Chassis base, 7 × 9 × 2 inches, BUD, CB-1182

8-quinolinol concentration of 2.0 to 10.0 grams per liter and a free acid concentration between 0.1 and 0.2 M. Take a 200-microliter aliquot with a micropipet and add to the titration vessel.

Other sampling can be used. The final cell solution should contain 0.4 to 2 mg. of 8-quinolinol, be 10^{-3} to 10^{-4} M in acid, and be 0.2 M in sodium bromide.

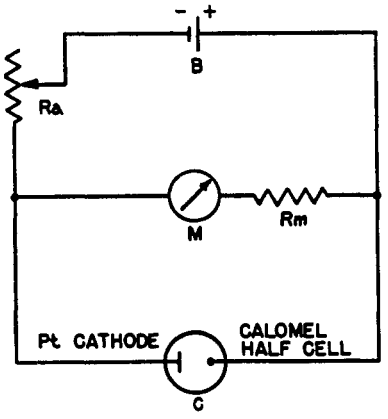

Figure 2. Indicator Circuit

M. Meter, 0–50 microamperes scale, Simpson Model 25 (~1000 ohms coil resistance)
Ra. 150,000-ohm potentiometer (adjusting resistor)
Rm. 9000-ohm, 1-watt (meter resistor)
B. Battery, 7.5-volt, Burgess W5BP
C. Cell

Titration. Adjust the constant current supply to give a current of 5 to 15 ma., and determine the value by measuring the IR drop across R-7 (Figure 1) with the potentiometer. Adjust the indicator meter current to approximately 25 microamperes, and turn on the electrolysis current. Allow 30 seconds for the indicator current to become steady, and then note its value to 0.1 microampere.

Continue the electrolysis until the indicator current decreases 2 microamperes below the stable starting value. Stop the electrolysis, and check the end point as follows: Wait 30 seconds and if the indicator current has risen more than 0.5 microampere, continue the electrolysis until the current again decreases to the original stop value. Observe the current for 30 seconds as above. Repeat until the current does not rise 0.5 microampere in 30 seconds. Note the time to 0.1 second. Check the end point further by continuing the electrolysis; the indicator current will decrease very rapidly if the true end point has been reached.

Calculations. The time in seconds multiplied by the current in milliamperes and divided by 96,500 gives the milliequivalents of bromine generated. This divided by 4 gives the milliequivalents of oxine in the aliquot. The final result can then be calculated as for ordinary titrations.

RESULTS

Titration of Standard Oxine Solutions. Standard solutions were made by dissolving various amounts of 8-quinolinol in hydrochloric acid and diluting as directed. Two hundred microliters of these solutions added to 50 ml. of 0.2 N sodium bromide gave a solution with an approximate pH of 3.5.

One solution was independently standardized by using a bromate-bromide mixture (standardized against Bureau of Standards arsenious oxide) to brominate the oxine, and titrating the excess bromine with 0.01 N thiosulfate, using starch and iodide as indicator. Large samples (50 ml.) were taken and precautions against loss of bromine observed. Four duplicate analyses made at different times gave eight results that agreed ±0.0010 in normality.

Table I gives the summary of the results of the titrations, most of which were performed by a laboratory assistant with no previous experience with the apparatus. The precision results are the "best estimate" of the standard deviation, computed from

$$\hat{\sigma} = \sqrt{\frac{\Sigma (dx)^2}{n-1}}$$

where dx is the deviation of individual values from the mean, and n is the number of determinations.

Table I. Titration of 8-Quinolinol Solutions

Av. Normality Obtained	Range of Normality	No. of Analyses	Precision		Amount of 8-Quinolinol, Mg.
			Normality	%	
0.2155[a]	0.2171–0.2143	14	±0.00098	±0.45	1.1
0.4001	0.4009–0.3989	12	±0.00067	±0.16	2.0
0.1755	0.1765–0.1745	11	±0.00075	±0.42	0.88
0.09536	0.09556–0.09485	11	±0.00025	±0.27	0.47

[a] Nominal value as determined by BrO_3^--Br^- titration 0.2156. Other solutions were not independently standardized.

DISCUSSION

Bromine is an ideal reagent to generate electrolytically, because the oxidation of bromide to free bromine at platinum electrodes is essentially 100% efficient. Side reactions at the electrode are not very probable in acid solutions; oxygen evolution and attack of the platinum electrode are not observed.

The indicator system used is very sensitive and gives a sharp break in the coulometric titration of arsenite ion with bromine. However, the rate of bromination of the 8-quinolinol is slow and makes the end point sluggish. Unsuccessful attempts to catalyze the bromination and thus improve the end point were made, using arsenic (V), iodine, iron (III), copper, and antimony (V). The initial current setting of 25 microamperes is not critical; any value between 15 and 50 microamperes will give good results. If the indicator current is not stable, the indicator electrode may be too close to the electrolysis anode or the stirring speed may be too low.

Conditions for the end point are critical. The end point is either very poor or unobtainable if the solution is very acid or very basic. An end point is obtained in solutions of pH 1.5 to 6.0 if the salt content is kept around 0.2 N. No end point was obtained in acetate, phosphate, or biphthalate buffers, presumably because of the high salt content. The optimum acidity was found to be pH 3 to 4, but the upper limit of the salt content was not determined. The several false end points obtained because of the slow bromination of the 8-quinolinol serve a useful purpose in that they warn of the approaching end point, and thus eliminate the need for a preliminary titration.

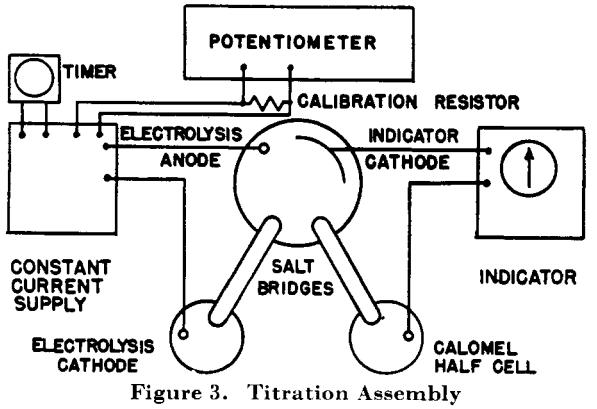

Figure 3. Titration Assembly

The dibromo derivative separates as a white flocculent precipitate during the electrolysis. A useful criterion for the suitability of an electrolyte for the titration was found during this study, in that no end point was obtained using solutions in which the dibromo derivative was soluble. This criterion was not investigated thoroughly, but it held for all cases observed.

The greatest uncertainty in the titration is the time of electrolysis. In spite of the sensitivity of the indicator, an error of 1 to 2 seconds can occur. Hence, the current used for electrolysis should be so chosen that the time of titration is long enough to

cause the relative error to be small. A titration time of 10 minutes would permit a 2-second error in the end point with an error of 0.3%.

ACKNOWLEDGMENT

The author wishes to express his thanks to W. T. E. Elmendorf for his help on the design of the constant current source, to S. A. Hays for his work on the indicator system, and to his co-workers for their help and advice, both in the conduct of the work and in the preparation of this report.

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RECEIVED January 24, 1950. Presented at the Northwest Regional Meeting, AMERICAN CHEMICAL SOCIETY, Richland, Wash., June 9 and 10, 1950.

NOTES ON ANALYTICAL PROCEDURES . . .

Colorimetric Determination of Molybdenum by Means of Nitric and Perchloric Acids

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IN GENERAL, the methods for the determination of small quantities of molybdenum are modifications of the procedure described by Marmoy (*3*), which is based on the amber color of the molybdenum thiocyanate complex formed when stannous chloride and potassium thiocyanate are added to a solution containing molybdenum. The color density is determined either directly or after the complex has been extracted with ether, as governed by interfering ions present and the molybdenum concentration.

In an effort to increase the accuracy of Marmoy's method, Nichols and Rogers (*4*) recommended the addition of 10 mg. of trivalent iron to each sample, because smaller quantities affect the color density of the molybdenum-thiocyanate complex. The silica residues from soil and plant samples were volatilized as silicon tetrafluoride. According to Sandell (*7*), silica residues should be fused with sodium carbonate to prevent loss of molybdenum. Robinson (*6*) modified the original method by using isopropyl rather than ethyl ether for extraction of the molybdenum complex, because its lower vapor pressure causes less loss from evaporation. Ellis and Olson (*2*) found that acetone was more effective than stannous chloride as a reducing agent when the color density of the molybdenum complex was determined directly in a 20-ml. volume of the unknown. But the evaporation of nitric-perchloric digestates of a sufficient quantity of plant material to a volume of 20 ml. causes precipitation of salts and a possible loss of molybdenum. Barshad (*1*) recommended that sodium nitrate be added in the determination to prevent molybdenum from being reduced to the valence below 5 that is necessary for the formation of the complex.

Certain methods for determining molybdenum in biological materials require that organic matter be destroyed by dry ashing. It was found in this laboratory that nitric and perchloric acid digestion was more convenient than dry ashing for plant tissues. The silica residues from wet digestions of plant tissues do not retain appreciable quantities of molybdenum and fusion or other treatment is, therefore, unnecessary. Less than 1 microgram of molybdenum was contained in the silica residues from twelve 6-gram digestions of alfalfa when combined and fused with sodium carbonate. In wet digestion, all traces of organic matter must be destroyed. Even though the digestate appears colorless, traces of organic materials induce a yellow color, in many cases, upon addition of ammonium thiocyanate and stannous chloride. To avoid this, the digestion mixture should remain overnight on a hot plate at a low temperature. When dryness is reached, hydrogen peroxide and additional quantities of nitric and perchloric acids are added. Ammonium thiocyanate proved more satisfactory as a reagent than the generally used potassium thiocyanate. High potassium concentrations cause precipitation of potassium perchlorate and loss of molybdenum through adsorption or through coprecipitation.

The following method employs the additional modifications found necessary to adapt the procedure for use on digestates of nitric and perchloric acids. This procedure is much more rapid than that of dry ashing, which is reported to require a fusion or other treatment of the silica residues.

DETERMINATION OF MOLYBDENUM IN PLANT TISSUE

Reagents required. Concentrated nitric and hydrochloric acids.

A 70% solution of perchloric acid.

A 30% solution of hydrogen peroxide.

A 10% solution of stannous chloride freshly prepared in 1 + 9 hydrochloric acid.

A 10% solution of ferric chloride (49 grams of ferric chloride hexahydrate per liter). Sodium nitrate solution, 5 *N*.

Standard solution containing 100 p.p.m. of molybdenum (0.150 gram of MoO_3) in 10 ml. of 0.1 *N* sodium hydroxide, made slightly acid and made up to 1 liter with water.

Isopropyl ether purified by shaking in a separatory funnel with one tenth its volume of a mixture containing one third each of the stannous chloride solution, ammonium thiocyanate solution, and water. Prepared freshly each day it is used.

PROCEDURE

Digest 1 to 10 grams of plant material containing from 1 to 20 micrograms of molybdenum by the nitric-perchloric digestion method described by Piper (*5*). Allow the digestion mixture to evaporate to dryness on a hot plate at low heat, then add 5 ml. of nitric acid and 1 ml. of perchloric acid and again evaporate to dryness. After the second evaporation, add 1 ml. of hydrogen peroxide and allow the mixture to go to dryness. When digestion is complete, add 70 ml. of water, boil approximately 1 minute, and add 10 ml. of concentrated hydrochloric acid. Filter and wash the filter with hot water, then allow to cool and make to 100 ml.

Transfer to a separatory funnel and add 5 ml. of the ammonium thiocyanate solution, 1 ml. of the sodium nitrate solution, 1 ml. of the ferric chloride solution, and 5 ml. of the stannous chloride solution. Mix, add exactly 10 ml. of ether, and shake 100 times. Allow the two layers to separate; draw off the aqueous phase and deliver the ether into a glass-stoppered flask or tube. If the sample contains 20 micrograms or more of molybdenum, return the aqueous phase to the separatory funnel and extract with a second portion of ether, and combine it with the first. Ten minutes after separation, determine transmittance with a spectrophotometer or colorimeter, using a covered cuvette. Maximum absorption is at 475 mμ. Wratten filters 47A and 45 are satisfactory. Prepare a standard curve, following the same procedure. Run a blank determination on each new group of reagents.