Table I. Compounds Suitable for Vapor Bath

Compounds	B.P., ° C.
Water	100
Toluene	110
Isoamyl acetate	142
p-Dichlorobenzene	174
Ethylene glycol	197
Methyl salicylate	223
Isoamyl benzoate	262
Diphenylamine	302
Benzyl benzoate	323
n-Butyl phthalate	340

Table II. Performance Data

Sample	B.P., ° C.	Molecular Weight	
		Theoretical	Experimental
Acetone	56.5	58	58
Benzene	80.1	78	79
Toluene	110.8	92	95
Chlorobenzene	132.0	113	114
Ethyl benzoate	212.6	150	153
Aniline	184.4	93	91

After the apparatus is assembled and checked, a liquid of suitable boiling point (see Table I) is placed in *G* and heated to boiling. This boiling is continued until no more mercury is expelled. If the temperature tends to climb slowly, a final temperature may be arbitrarily chosen, provided the flame is removed immediately after the reading is taken. When the final temperature is noted, the height of the vertical column of mercury as measured from the meniscus in the vaporizer to the level of the orifice of the capillary outlet at *E* is also recorded.

The usual corrections for the expansion of the mercury and the air error are made by means of a blank run, using an empty weighing capillary. It has been the practice to run a blank for each bath liquid used. The average correction per degree change in temperature can be calculated from one such run and applied in the way described by Niederl. Other corrections also are handled as in Niederl's method.

After completion of the run, the apparatus may be quickly cleaned out and made ready for the next run by the following procedure. A suction-flask assembly that connects with ball joint *E* via a socket joint is clamped into place. Suction is applied, stopcock *H* is opened, and the mercury in the vaporizer unit is pulled into the suction flask. The constant-temperature bath is operated during this process so that the sample remains vaporized and may be evacuated as the mercury is being drawn off. By successively opening and closing stopcock *H*, it is possible to flush the vapors of the sample from the vaporizer quantitatively. If need be, a solvent can be flushed through the vaporizer by introduction through joint *A*. The old weighing capillary may then be removed and the apparatus is ready for the next run.

RESULTS

The excellent performance of this apparatus is illustrated by the results in Table II, which were obtained by a senior chemistry student who had had no previous experience with this apparatus.

These results were obtained on samples of 10 to 15 mg. weighed on a good analytical balance. Although the use of a microbalance might have given closer results in some cases, those given here are typical of the many determinations run. The capacity of the apparatus described is such that larger samples might readily be used. With water as the liquid used in the vapor bath, an 11-mg. sample of acetone displaced only one third of the available capacity.

Because the primary utility of such an apparatus as this is in the straightforward and rapid determination of molecular weights, the vapor bath has been employed throughout. A liquid bath can be easily substituted, if the boiling and condensation points of a liquid are desired.

LITERATURE CITED

(1) Niederl and Niederl, "Organic Microquantitative Analysis," 2nd ed., New York, John Wiley & Sons, 1942.

RECEIVED April 10, 1950.

Quantitative Determination of Bromine in Terminal Bromodinitromethyl Groups

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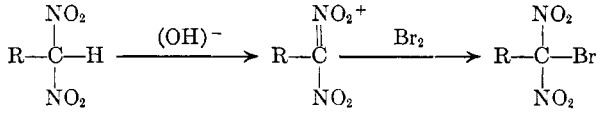
THE study of compounds with terminal dinitromethyl groups made it desirable to find a facile laboratory method for their characterization. Compounds with terminal dinitromethyl groups are readily brominated in basic solution to form the corresponding bromodinitro derivative. Because the bromodinitro derivatives are easily prepared and purified, halogen analysis of these compounds seemed to offer a convenient method for the quantitative determination of terminal dinitromethyl groups.

Table I. Determination of Bromine

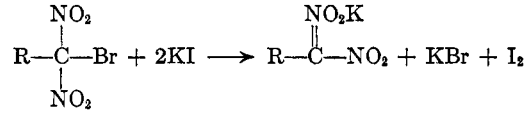
	Compound	%Br Calcd.	%Br Found	% Dinitromethyl Group Calcd.	% Dinitromethyl Group Found
1	$Br-C(NO_2)_2-CH_2CH_2COOCH_3$	29.49	29.58 29.92	38.75	38.88 39.33
	$Br-C(NO_2)_2-CH_2CH_2COOH$	31.10	31.06 31.29	40.87	40.83 41.12
3	$Br-C(NO_2)_2-CH_2OH$	37.17	36.85	48.86	48.43
4	$Br-C(NO_2)_2-Br$	60.57	60.19 59.89	...	...
5	$CH_3-C(NO_2)_2-Br$	40.16	40.11 40.08	52.79	52.72 52.68



Two methods of halogen analysis appeared worthy of consideration: treatment of the compound with an alkaline reagent, followed by titration of the ionic halogen with silver nitrate; and treatment of the compound with potassium iodide in the manner reported by Meisenheimer (*1*) for 2-bromo-2,2-dinitro-1-ethoxyethane, followed by titration of the free iodine with sodium thiosulfate.

The first method was found unsatisfactory. In order to obtain the halogen in ionic form, it was necessary to treat the compound with an alkaline reagent in an organic solvent. Colored solutions resulted from this operation, which obscured the end point of the silver nitrate titration.

The reaction of compounds with terminal bromodinitromethyl groups and potassium iodide proceeded quantitatively. For every compound investigated, the amount of iodine formed corresponded to the theoretical amount of bromine present in the molecule according to the following equation:



The percentage of bromine in a compound may be expressed by the formula,

$$\frac{79.92 \times N \times V}{2 \times 10 \times W}$$

where V = milliliters of sodium thiosulfate, N = normality of sodium thiosulfate solution, and W = sample weight in grams.

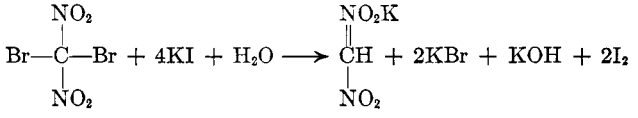
The percentage of terminal dinitromethyl groups can be obtained readily from the same formula by substituting the formula weight of the dinitromethyl group, 105.04, for that of bromine, 79.92.

Table I shows the results obtained with this analytical method.

EXPERIMENTAL

General Procedure. To 0.2 to 0.3 gram of the bromodinitro compound dissolved in 25 ml. of methanol are added about 2 grams of potassium iodide. Free iodine is liberated at once and after a few seconds the mixture is diluted with 25 ml. of water. Then the free iodine is titrated with 0.1 N sodium thiosulfate solution in the usual manner, using starch indicator.

Titration of Dibromodinitromethane and Compounds Having Basic Amino Groups. Upon reaction of dibromodinitromethane with potassium iodide, the solution becomes alkaline according to the following equation:



It is necessary to neutralize the solution with dilute sulfuric acid to a pH of 6 to 7 before titration with sodium thiosulfate. The same is true of the titration of compounds containing substituted amino groups, which cannot yet be tabulated because they are still classified. A better end point is obtained in neutral solution; therefore acidification is necessary only in these two cases.

LITERATURE CITED

(1) Meisenheimer, *Ber.*, 36, 434 (1903).

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Analysis by Permanganate Titrations of 8-Quinolinols

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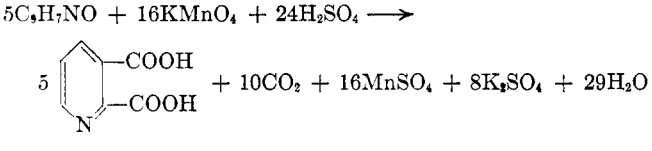
ALTHOUGH a permanganate titration method for determining metals with 8-quinolinol has been known for a long time (*1*), the procedure is stated to be empirical and not sufficiently well investigated to be very useful. Therefore this method has been reinvestigated.

By the modifications specified in the experimental procedure below the reaction can be made to correspond to a feasible equation over a narrow range of conditions if an excess of standard permanganate is added and back-titrated, after some time has been allowed for the reaction to be completed, with iodide and thiosulfate. The equation used for the calculation of the results was as follows:

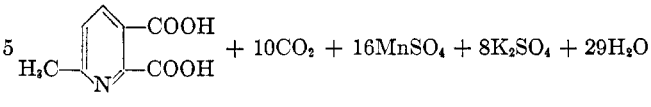


The average error in the determination of seventeen samples of pure 8-quinolinol ranging in size from 13.0 to 29.0 mg. was 0.4 mg.; the length of time allowed for the reaction was 15 minutes and the excess of permanganate about 2 ml. The reaction time and the amount of excess permanganate must be carefully controlled, because the results become progressively higher with longer times and larger excesses than those stated—for example, the results are about 10% high when either the time for the reaction or the excess of permanganate is doubled. Although this indicates that the oxidation proceeds farther than the equation provides for, no limit to the extent of oxidation could be obtained within the range of conditions usable for practical analysis. Evidently the determination is empirical, but is stoichiometric with the equation written when the conditions are controlled as specified.

The procedure was applied to the analysis of seven synthetic copper samples with the results shown in Table I.

Presumably, results of the same order of accuracy would be obtained in the determination of other ions quantitatively precipitated by 8-quinolinol.

Although this method may be satisfactory for many purposes, it was found that the similar titration using 8-hydroxyquinaldine in place of 8-quinolinol was much better, in that the range of conditions over which the reaction obeyed the equation



seemed to be unlimited, in spite of the fact that the products in the equation as written are probably not the true products of the reaction.

Table I. Copper Determination by Permanganate Titration of 8-Quinolinol

% Cu Present	% Found	% Cu Present	% Found
7.38	7.36	4.84	5.07
8.97	9.29	6.90	7.09
8.28	8.59	7.67	7.87
8.67	8.90		

The analysis of seventeen samples of pure 8-hydroxyquinaldine ranging in size from 13.0 to 31.7 mg. gave values correct to 0.3 mg. or better in every trial, even when the quantity of excess permanganate and the length of time allowed for the reaction varied widely. This reaction appears to be truly stoichiometric rather than empirical, in contrast to the similar reaction of 8-quinolinol. The procedure was applied to the analysis of prepared magnesium samples with the results shown in Table II.

EXPERIMENTAL

Reagents. 8-Quinolinol was purified by recrystallization from alcohol; 8-hydroxyquinaldine was prepared and purified as previously described (*2*).