Quantitative Separation of Phenol from the Cresols and Higher Phenols[1]

J. N. Miller and O. M. Urbain

URBAIN LABORATORIES, COLUMBUS, OHIO

A method for the quantitative separation of phenol from related substances is given. The phenol is quantitatively destroyed and is then determined by difference, using any method that accurately measures all phenolic substances present.

THIS paper describes a procedure for the quantitative separation of phenol (monohydroxybenzene) from the cresols and higher phenols usually present with phenol in biological fluids, polluted water supplies, etc. Such a method of separation is desirable because at certain times it is necessary to know the exact phenol content irrespective of the cresols or higher phenols present. The determination of small amounts of phenol in the presence of these other bodies has hitherto been difficult because the most sensitive color reactions given by phenol are also given by most of the related compounds. The production of the indophenol dyes and other colored compounds for the colorimetric estimation of phenol gives a measure, not of the phenol alone, but of all substances present entering into similar reactions. As these dyes are highly colored, they constitute the most sensitive chemical tests for phenol, concentrations as low as a few thousandths of a milligram in a liter being readily measured. This method of separation leaves the choice of a procedure for the determination of the phenol following its separation up to the investigator who knows the requirements of the case in hand.

The method here described depends on the fact that the cresols and higher phenols, in short all phenolic substances in which the phenol hydrogen is not replaced, are not oxidized by the chromic acid mixture, while phenol is itself quantitatively broken down. The figure for the phenol is obtained from the difference between that for all the phenolic bodies present simulating phenol in the reaction used and that obtained after the phenol has been destroyed. The ultimate standard for the determination is a phenol solution of known concentration treated in exactly the same manner as the unknown is treated.

In the experimental work that follows a modified form of the Fox and Gauge (*1*) method of measurement is used. This method produces a highly colored azophenol dye salt through the action of diazotized sulfanilic acid and sodium hydroxide. The color of the dye salt produced by this method is easily matched with permanent platinum-cobalt color standards, a distinct advantage when a series of determinations, such as the following, is to be made.

As the method of separation calls for two determinations, one of the total phenolic substances giving the reaction of phenol present and one of all of these substances minus only the phenol, the procedure of running the two in parallel is followed. This is to say, two portions of the sample to be analyzed are taken and each is placed in apparatus of the same type and subjected to the same treatment except that the phenol is destroyed in one and not in the other.

Apparatus

After experimenting with apparatus of a number of types, the writers finally selected that which is used in the Kjeldahl nitrogen determination as being the simplest and most suitable. In Figure 1 the details of the two sets of apparatus are given. They consist of 500-ml. digestion flasks (*A*), Kjeldahl steam traps (*B*), 60.96-cm. glass Liebig condensers (*C*), and 250-ml. graduated cylinders (*D*). The stoppers used for fitting the traps to the flasks and condensers are tin-foil-covered corks free from cracks.

A zero blank could not be obtained on an apparatus using a rubber stopper of any type. This was especially true when the stoppers had been in contact with phenol vapors or solutions a number of times. In some instances corks gave blanks, but in no instances were blanks obtained when tin-foil-covered corks were used.

Reagents

(1) A saturated solution of chromium trioxide in sulfuric acid. This is prepared by placing a quantity of chromic acid crystals, about twice the amount that will go into solution, in a glass-stoppered bottle and adding concentrated sulfuric acid. It is shaken from time to time over a period of several days and is then ready for use.

(2) An 8 per cent by weight solution of recrystallized sulfanilic acid containing 1 ml. of concentrated sulfuric acid in 250 ml. of solution. This solution is easily kept for several weeks.

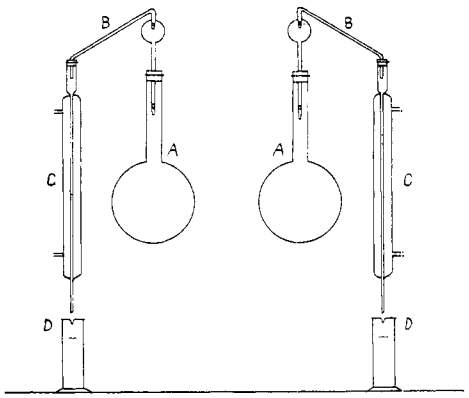

Figure 1

(3) A freshly prepared 8 per cent by weight solution of sodium nitrite.

(4) A 10 per cent solution of sodium hydroxide.

(5) A standard phenol solution. This is best prepared as used by diluting a stronger solution containing about 1 gram of pure phenol per liter. This stock solution can be carefully standardized by any of the methods suitable for determining large amounts of phenol.

Analytical Procedure

Divide the sample into two 250-ml. portions and place in the flasks (*A*). When smaller amounts of sample are to be had they can be diluted to a known extent and an aliquot part taken for the analysis. Next add 3 ml. of concentrated sulfuric acid to the contents of each flask. This is to render

[1] Received October 25, 1929.

volatile all of the phenol. Then connect the flasks to the condensers and place the graduates in position to receive the distillates. Apply heat and catch 240 ml. of distillate in each case. Now put aside these distillates while the flasks and condensers are cleaned and rinsed with distilled water. Return the portions of distillate to their respective flasks. To No. 1 add 10 ml. of the chromic acid solution mentioned and to No. 2 add 10 ml. of sulfuric acid. Connect the flasks to the condensers and apply such heat as will bring the contents of each to the boiling point in from 40 to 45 minutes. As soon as the boiling point is reached, remove the flames. Let the contents of the flasks stand hot for 30 minutes. During this time, if sufficient care has been taken in bringing the solutions just to the boiling point, no more than a few drops of distillate will have passed over, most of the steam formed having condensed in the bulbs of the steam traps. Following the period of standing, apply the full flame and collect 225-ml. portions of distillate.

No. 2 graduate now contains all of the phenolic bodies simulating phenol plus the phenol. No. 1 graduate contains no phenol but all the other similar bodies. The difference between the contents of the two graduates in terms of a standard phenol solution which has received the same treatment as portion No. 2 of the sample will be the phenol content of the sample.

To develop the color in the two portions by the method of measurement used in these experiments, treat 50 ml. of each with 4 ml. of the sulfanilic acid solution and then with 2 ml. of the sodium nitrite solution. This can be done in Nessler tubes or any suitable vessel. After a thorough mixing, add 5 ml. of sodium hydroxide and mix again. The full color is developed in about 3 minutes. Making the comparisons in a colorimeter greatly adds to the sensitivity of the determination.

When a number of determinations are to be made it is advisable to distil a portion of a standard phenol solution having relatively the same phenol content as the unknowns and to match the color produced in the distillate with a platinum-cobalt color solution. The latter affords a permanent standard with which all comparisons can be made in a colorimeter.

The accuracy of the method has been tested in the presence of a variety of phenolic substances over a range of from 0.010 to 10.00 mg. of phenol per liter. The procedure followed was to start with a portion of a standard phenol solution and to add to this varying amounts of the cresols, resorcinol, and quinol. This standard solution containing these substances was then analyzed for its phenol content. The results obtained are given in Table I.

Table I

Phenol Present	Other Substances Present	Phenol Found	Error
Mg. per liter		*Mg. per liter*	*Mg. per liter*
0.010	*o*-, *m*-, *p*-Cresol-[a]	0.017	+0.007
	p-Cresol, resorcinol	0.012	+0.002
	Nothing	0.004	−0.006
0.015	*o*-Cresol	0.016	+0.001
	o-Cresol, resorcinol	0.018	+0.003
	o-Cresol, quinol	0.015	0.000
0.100	*o*-, *p*-Cresol	0.098	−0.002
	Nothing	0.105	+0.005
	Resorcinol	0.104	+0.004
0.500	*o*-, *m*-Cresol	0.497	−0.003
	p-Cresol	0.511	+0.011
	p-Cresol	0.502	+0.002
1.000	Nothing	0.99	−0.01
	m-Cresol	0.99	−0.01
	o-, *p*-Cresol, quinol	1.00	0.00
2.500	Quinol, resorcinol	2.51	+0.01
	p-Cresol	2.47	−0.03
	Nothing	2.50	0.00
5.00	*p*-, *m*-, *o*-Cresol	5.07	+0.07
	Nothing	5.08	+0.08
	Resorcinol	4.91	−0.09
10.00	Nothing	10.02	+0.02
	o-Cresol, resorcinol	10.01	+0.01
	Quinol, resorcinol	9.96	−0.04

[a] The amount of these other phenolic substances added was approximately 2 mg. per liter in each case.

Analytical Results

It may be seen that the presence of the cresols or other phenolic substances in no way interferes with the determination of the phenol by this method. When no other substances were added to the phenol solutions the deviations from the theoretical values were of approximately the same magnitude as when these substances were present.

It might be well to state again that this method of separation can be used with any volumetric, colorimetric, or other scheme for measuring the phenol. The amount of chromic acid mixture required for concentrations of phenol higher than those used here has not as yet been determined. It is, however, reasonable to suppose that higher phenol concentrations will require more than 10 ml. of this reagent to bring about complete oxidation. More chromic acid would also probably be required when large amounts of oxidizable organic matter other than phenol were present in the unknown. These phases of the method are now under investigation in the writers' laboratory.

Literature Cited

(1) Fox and Gauge, *J. Soc. Chem. Ind.*, **39**, 260 (1920).

Rapid Volumetric Method for the Determination of Lead[1]

R. C. Wiley

University of Maryland, College Park, Md.

THE basis for the following method for the determination of lead is Alexander's molybdate method. In the past when lead salts have been titrated against ammonium molybdate, tannic acid has been largely used as an indicator to determine when an excess of the molybdate was present. In some cases the end point was determined by noting the point at which no further precipitation of lead took place upon addition of ammonium molybdate. In the method here described a mixture of stannous chloride and potassium thiocyanate dissolved in water is used.

[1] Received October 18, 1929.

Epperson (*1*), in the determination of molybdenum, titrated the molybdenum solution against a standard lead solution, using tannic acid as an indicator. He found the results satisfactory when extreme accuracy was not required.

Kedesy (*2*) claims that an excess of stannous chloride in the stannous chloride thiocyanate reagent will prevent color from forming when molybdate is added.

Weiser (*4*) notes that lead molybdate is best precipitated from a solution slightly acid with nitric acid. To complete the precipitation the solution is made alkaline with ammonium hydroxide and then just acid with acetic acid.