

## THE DETERMINATION OF PHENOLS BY THE RING-OVEN TECHNIQUE

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**Abstract.** A simple, quick, precise and sensitive method for the determination on cresol, resorcinol, phloroglucinol, hydroquinone and pyrogallol has been devised using the Ring-Oven Technique. Effect of interferences has also been studied. Shelf life of the standard scale has also been investigated. The method reported is practicable even for the determination of phenols in polluted water.

Scientific research has whole heartedly bent its attention in demolishing air pollution. Phenol pollution is harmful to human skin,<sup>1</sup> its unpleasant odour and taste being experienced particularly in chlorinated water supplies.<sup>2</sup> It draws much needed attention for devising some rapid, simple, quick, precise and sensitive method for the determination of phenols.

In our previous communication<sup>3</sup> the Weisz Ring-Oven Technique has been employed for the determination of phenol. In the present paper the scope of the method has been extended to the determining of five other phenols. The colour reaction of amino-antipyrine and potassium ferricyanide with phenols<sup>4-7</sup> has been utilized again for their determination and some of the result of this investigation are reported here.

### Experimental

#### Reagents

Aqueous solutions of resorcinol (E.Merck), pyrogallol (E.Merck), Hydroquinone (Reidel De Haen), *o*-cresol (Reidel De Haen) and phloroglucinol (L.Light and Co. Ltd. Coinbrook, England) were prepared separately by dissolving 1 g each of them in 100 ml of water respectively. Exact dilutions of the above solutions were made for low concentrations.

**Amino-Antipyrine.** A 0.2 % aqueous solution of amino-antipyrine (KOCH-Light Labs., England) was prepared.

**Potassium Ferricyanide** Dissolved 2 g of potassium ferricyanide (analytical grade) in water to which 5 ml of 1 M NaOH was also added and the final volume was made to 100 ml with water.

#### Apparatus

Weisz Ring-Oven (made by the electronics section of

the PCSIR Laboratories, Lahore) with 110° working temperature, Whatman filter paper No. 41 and automatic capillary pipettes of 1  $\mu$ l and 2  $\mu$ l capacity (M/s. Karl Kolb. Scientific and Technical Supplies, Buchschlag-Frankfurt, W. Germany) were used.

#### Procedure

At the centre of Whatman filter paper No. 41, 1  $\mu$ l of phenol test solution and 2  $\mu$ l of amino-antipyrine were applied with automatic capillary pipettes and the paper was allowed to dry in air for about 2 min. Then 1  $\mu$ l of potassium ferricyanide was transferred at the spot of the paper where previously two other solutions were added. The coloured compound thus produced was washed with water into the ring zone on the ring oven, whose temperature, as mentioned earlier was maintained at 110°. Ten washings were sufficient for complete washing of the reaction product to the ring zone. Three rings, with varying volumes of each test phenol solution were prepared. These were evaluated against the standard scale prepared by taking different volumes i.e. 1,2,4,6,8 and 10  $\mu$ l of the respective standard phenol solution. The results were calculated according to the known method.<sup>8</sup> This method was followed for all the phenols under test. The strengths of all the unknown solutions of the phenols under examination, were found according to Weisz's method.<sup>8</sup>

Shelf life of the once prepared standard scale was checked at regular intervals by evaluating known solutions according to the above method.

#### Interferences

The following method was employed for studying the effect of the interferences on the determination of phenols.<sup>9</sup>

A ring (I) containing 1  $\mu$ l of the interfering sub-

stance, another ring (II) containing 1  $\mu$ l of phenol and 1  $\mu$ l of the interfering substance were prepared according to the method described above. The substance was confirmed non-interfering if the ring (I) matched with the blank(III) and the ring(II) matched with the standard ring containing the same amount of the test phenol as itself.

### Results and Discussion

Amino antipyrine is a sensitive reagent for the determination of phenols. A red colour is produced immediately when phenol, amino antipyrine and alkaline ferricyanide are applied on the paper. Out of the various solvents tried, 8 to 10 washings with water proved to be the most suitable for washing the coloured reaction product to the ring zone.

The sensitivity of the method is apparent from the results reported in Table 1. Phenols in as low concentrations as 200.00  $\mu$ g each of resorcinol and pyrogallol, 300.00  $\mu$ g hydroquinone, 400.00  $\mu$ g phloroglucinol and 500.00  $\mu$ g cresol per ml can be determined accurately by this method. In order to further improve the detectible limits of these phenols in their solutions with concentrations lower than those mentioned in the work, it was found that larger sample aliquots may be applied in a way that each 2-3  $\mu$ l sample solution transferred to the paper be dried with hot air before making further additions. This procedure should be continued till the required volume of the solution is transferred. This is done to keep the area occupied by such solution within reasonable limits i.e. it should be much within the boundaries of the final ring. By this method we improved sensitivity of the method even ten times more than the results reported in Table 1, but the method then becomes a little bit time consuming because one has to spend sufficient time to transfer the required volume of the test solution.

However, where these all five phenols can be individually determined with reasonable accuracy they seriously interfere with each other's determination, which was done according to the method of Dharmarajan and West.<sup>9</sup>

TABLE 1. DETERMINATION OF PHENOLS.

Substance	Amount taken	Amount found	Error %
Resorcinol	200.00 $\mu$ g/ml	204.00 $\mu$ g/ml	+2.00
	350.00 " "	334.00 " "	-4.57
	450.00 " "	434.00 " "	-3.55
	600.00 " "	566.00 " "	-5.67

continued

(Table 1 continued)

	800.00 " "	742.00 " "	-7.25
	900.00 " "	860.00 " "	-4.44
	950.00 " "	914.00 " "	-3.79
	1.00 mg/ml	970.00 " "	-3.00
	1.10 " "	1.13 mg/ml	+2.73
	1.30 " "	1.26 " "	-3.07
Pyrogallol	200.00 $\mu$ g/ml	197.40 $\mu$ g/ml	-1.30
	410.00 " "	415.00 " "	+1.22
	660.00 " "	634.00 " "	-3.94
	790.00 " "	742.00 " "	-5.95
	890.00 " "	860.00 " "	-3.37
	990.00 " "	940.00 " "	-5.05
	1.30 mg/ml	1.20 mg/ml	-7.69
	1.57 " "	1.48 " "	-5.73
	1.63 " "	1.60 " "	-1.84
	1.87 " "	1.82 " "	-2.67
Hydroquinone	300.00 $\mu$ g/ml	310.00 $\mu$ g/ml	+0.33
	560.00 " "	534.00 " "	-4.64
	650.00 " "	600.00 " "	-7.69
	760.00 " "	700.00 " "	-7.89
	830.00 " "	880.00 " "	-6.02
	950.00 " "	902.00 " "	-5.05
	1.17 mg/ml	1.11 mg/ml	-5.12
	1.25 " "	1.20 " "	-4.00
	1.39 " "	1.28 " "	-7.91
	1.53 " "	1.45 " "	-5.22
Phloroglucinol	400.00 $\mu$ g/ml	377.00 $\mu$ g/ml	-5.75
	550.00 " "	534.00 " "	-2.90
	650.00 " "	665.00 " "	+2.30
	850.00 " "	800.00 " "	-5.88
	950.00 " "	866.00 " "	-8.84
	1.13 mg/ml	1.15 mg/ml	+1.76
	1.25 " "	1.20 " "	-4.00
	1.36 " "	1.31 " "	-3.67
	1.50 " "	1.44 " "	-4.00
	2.00 " "	1.91 " "	-4.50
Cresol	500.00 $\mu$ g/ml	515.00 $\mu$ g/ml	+3.00
	650.00 " "	623.00 " "	-4.15
	700.00 " "	666.00 " "	-4.85
	800.00 " "	770.00 " "	-3.75
	880.00 " "	888.00 " "	+0.91
	975.00 " "	952.00 " "	-2.35
	1.00 mg/ml	0.93 mg/ml	-7.00
	1.25 " "	1.21 " "	-3.20
	1.37 " "	1.29 " "	-5.83
	1.50 " "	1.42 " "	-5.33

Interference by foreign ions was checked and it was found that sodium, potassium and calcium each in 100 fold excess to phenol, magnesium in 50 fold excess to phenol, manganese, zinc and copper each in 40 fold excess to phenol, ferric 1:1 and ferrous 1:0.5 ratio to phenol; chloride, sulphate, carbonate, bicarbonate, nitrate and thiocyanate each in 100 fold excess to

phenol flouride in 50 fold excess to phenol, phosphate in 15 fold excess to phenol and hydrazine in 50 fold excess to phenol do not interfere with the determination of phenols.

TABLE 2 STABILITY OF THE STANDARD SCALE.

Substance	Number of days	Amount taken mg	Amount found mg	Error %
Resorcinol	1	1.25	1.23	-1.60
	2	0.40	0.38	-5.00
	3	1.80	1.75	-2.78
	4	3.50	3.20	-8.57
	5	4.20	3.68	-12.38
Pyrogallol	1	0.20	0.20	+0.00
	2	1.50	1.41	-6.00
	3	2.25	2.41	+6.22
	4	3.80	3.49	-8.16
	5	4.95	4.21	-14.96
Hydroquinone	1	0.30	0.29	-3.33
	2	0.85	0.81	-4.70
	3	2.25	2.12	-5.78
	4	3.50	3.23	-7.29
	5	3.75	3.55	-8.00
	6	5.25	4.42	-15.57
Phloroglucinol	1	1.00	0.96	-4.00
	2	1.75	1.65	-5.71
	3	0.60	0.57	-5.00
	4	2.50	2.35	-6.00
	5	3.75	3.45	-8.00
	6	4.25	3.75	-11.76
Cresol	1	0.50	0.50	+0.00
	2	1.50	1.45	-3.33
	3	1.80	1.76	-2.22
	4	2.00	1.85	-7.50
	5	2.50	2.30	-8.00
	6	3.00	2.60	-13.33

Attempt was made to determine various phenols from a double distilled water sample to which phenols (individually) and the above impurities were added in known amounts within the permissible limits and it was found that these phenols were conveniently determined with the accuracy and precision as shown in Table 1.

Stability of the standard scale was also checked and as obvious from the results shown in Table 2, it is stable for four days in case of resorcinol and pyrogallol while for cresol, phloroglucinol and hydroquinone it is stable for five days. This life is quite suited to their routine analysis.

The method reported here is quite simple, easy to operate, accurate, quick, precise and sensitive. It is quite convenient and practicable where these phenols are to be determined individually. It is also suitable for routine analysis of total phenol contents in the presence of other element/substances reported above. Moreover, the apparatus used here is inexpensive and convenient to handle.

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