

## A RAPID CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF COAL ASH

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The various macrochemical methods for determining the composition of coal ash are time consuming and laborious. In this paper, a chromatographic method is discussed which is both rapid and simple. A new solvent system has been developed which not only saves time but also gives better  $R_f$  values, and is found to be very useful for quantitative estimation of rare elements like titanium, even when they are present in traces. This method could be applied for the analysis of other minerals also.

### Introduction

The chemical composition of ash from different coal samples is a subject of growing importance, since its composition reflects upon its behaviour during combustion. Besides this, there are reports in the literature <sup>1,2</sup> to show that coal ash could be a source for extracting radioactive and such rare elements as germanium, gallium, and titanium etc.

The usual macromethods<sup>3</sup> for ash analysis are tedious and time-consuming, and require large quantities of chemicals and special types of apparatus. Another disadvantage of these methods is that unless a certain element is present in appreciable quantity it can not be estimated accurately, and, if the reagents do not give a definite colour with an element such as alkali metals, alkaline earths and aluminium etc., the situation becomes worse.

Now-a-days, when the microtechnique is being applied in every field, an attempt has been made to adopt paper chromatography for the determination of various cations in the coal ash. This technique is easier, time-saving and sensitive, and requires very small quantities of the sample and the reagents. An instance in this connection is that the presence of lead which could not be reported, by applying macromethods in this laboratory previously, has been established in almost every sample using the present technique. The results were further confirmed by physical methods such as spectroscopy.

Three different techniques of paper chromatography e.g. disc, ascending and descending, were tried in different solvent systems and with different grades of paper in order to obtain better results.

### Experimental

Since the disc chromatography is the least time-consuming and does not require any special apparatus for development (a large dessicator may do), it was applied first using the following solvent systems:—

- (a) 90 vols. ethanol, 10 vols. 5N HCl<sup>4</sup>.
- (b) 80 vols. ethanol, 20 vols. 2N CH<sub>3</sub>CO-OH<sup>5,6</sup>
- (c) 50 vols. *n*-Butanol, 48 vols. ethanol, 2 vol. HCl.

In all the three cases Whatman No. 1 filter paper was used and the solvent system (a) gave better results when a known mixture was analysed. On applying to coal ash, no satisfactory results were, however, obtained. In systems (b) and (c) there was much diffusion.

Ascending chromatograms were prepared in the following solvent systems using the same Whatman No. 1 filter paper:—

- (a) 90 vol. ethanol, 10 vol. 5N HCl<sup>4</sup>
- (b) 80 vol. ethanol, 20 vol. 2N CH<sub>3</sub>COOH<sup>5,6</sup>
- (c) 90 vol. ethanol, 90 vol. isopropanol, 20 vol. 5N HCl<sup>7</sup>
- (d) 25 vol. methanol, 75 vol. CH<sub>3</sub>COOH<sup>8</sup>

A chromatogram usually took 2-3 hours for development. Best separation was obtained with solvent system (a). The only disadvantage in this system was the limitation of the solvent front and the transverse diffusion on prolonged standing for increasing the height of the solvent front. With solvent system (b) diffused spots were obtained and (c) gave streaks. In solvent system (d) the separation was poor and diffused.

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Descending chromatography was found to be most satisfactory and promising. The following solvent systems were applied:—

- (a) 100 vol. butanol, 100 vol. N HNO<sub>3</sub>, 5% acetoacetic ester<sup>9</sup>
- (b) 90 vol. ethanol, 10 vol. 5N HCl<sup>4</sup>
- (c) 80 vol. ethanol, 20 vol. 2N CH<sub>3</sub>COOH<sup>5,6</sup>
- (d) 90 vol. butanol, 90 vol. isopropanol, 20 vol. 5N HCl<sup>7</sup>
- (e) 50 vol. butanol, 48 vol. ethanol, 2 vol. HCl

In solvent system (a) the separation was satisfactory, but due to the higher concentration of iron, its spot occupied a larger area. The  $R_f$  value of iron is 0.13 in this system which is very close to the  $R_f$  values of other constituents which are expected to be present. (The  $R_f$  values of 15 common cations range from 0.11 to 0.15). The solvent (b) gave higher  $R_f$  values but the spots of Cd, Zn, Hg etc. were found at the solvent

front. With (c) diffused spots with poor separation were obtained. Alkaline earths, Ni, Co, and Al were better separated in solvent (d) but  $R_f$  values of Fe, Zn, Cd and Hg were found to be equivalent to 1 as in (b). On considering the results of (a) and (b) solvent systems a new solvent (e) was prepared. This system gave very promising results. The  $R_f$  value of Fe (+ + +) which was 0.13 in (a) and 0.9 in (b) became 0.5 and that of Zn, Cd and Hg ranged between 0.6 to 0.9. Moreover it takes about 17 hours to reach a distance of 35-40 cm. which is very reasonable. If the chromatogram is placed for development at 4 p.m. in the evening it can be taken out for analysis at 9 a.m. in the next morning.

The chromatograms developed by the above-mentioned solvents were prepared on Whatman No. 1 filter paper. Other papers were also used with solvent (e). The Whatman No. 3 was found to be almost similar to No. 1 except that the rate of flow is a bit fast and it requires larger quantities of solvent and reagents due to its thickness. Two

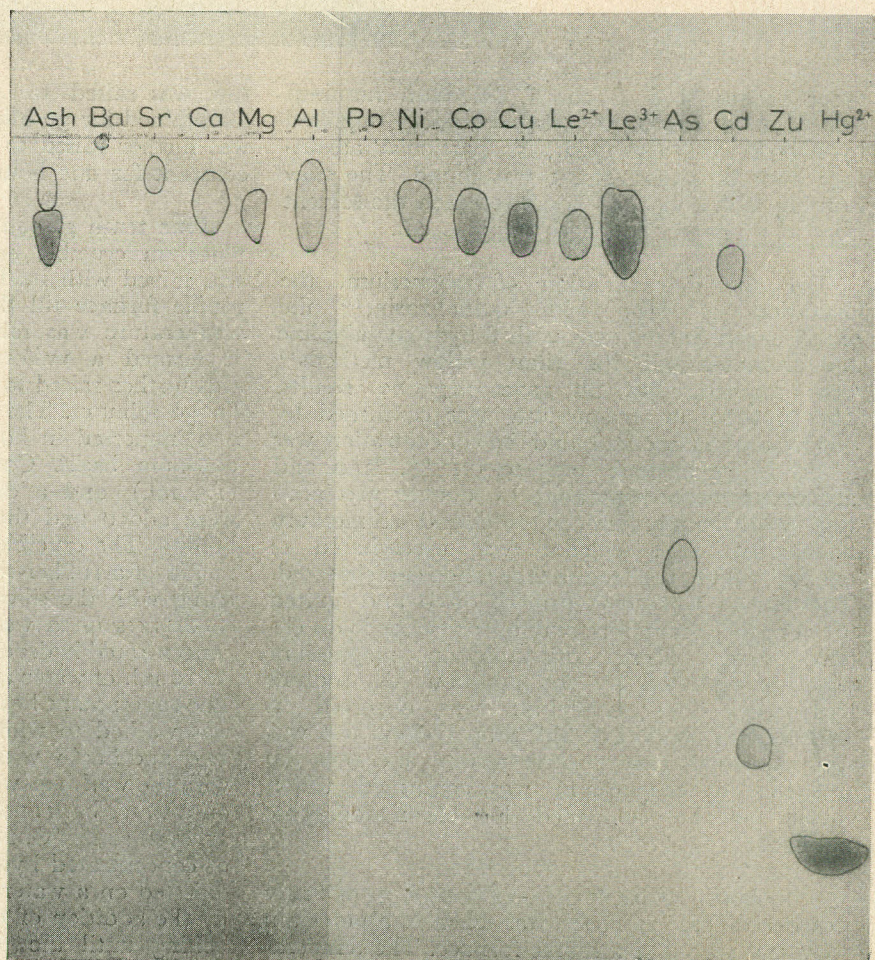


Fig. 1.—Separation using butanol N nitric acid and acetoacetic ester

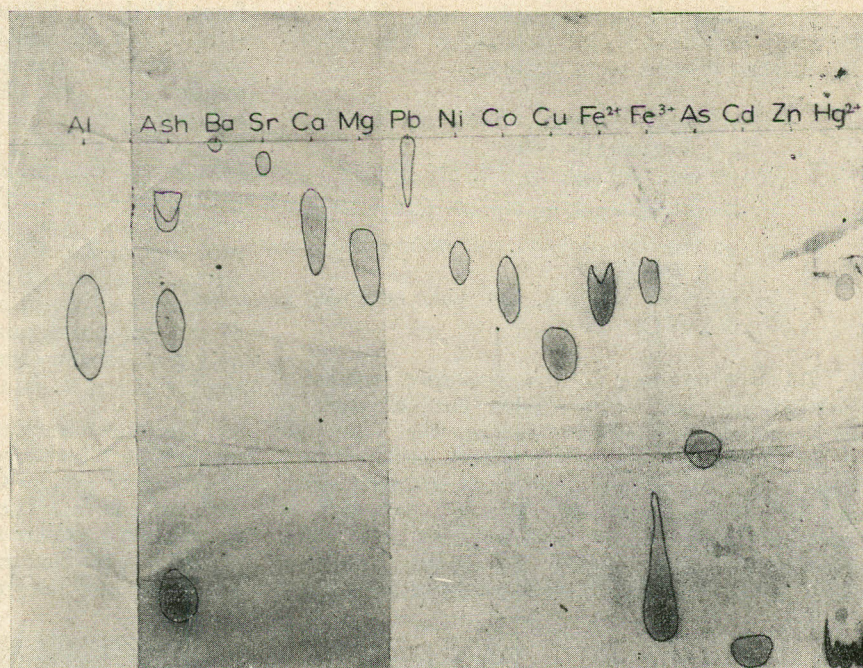


Fig. 2.—Separation using ethanol and hydrochloric acid.

other papers, S & S 2043a, (medium running) and S & S 2045b M, (slow running) supplied by Merck were also used. No particular advantage over Whatman No. 1 was found. The slow running took about 48 hours to reach the solvent front at a reasonable length of 35-40 cm.

For the determination of magnesium, the formation of lake with quinalizarin,<sup>10</sup> the bluish green fluorescence with 8-hydroxyquinoline and ammonia and the titan yellow methods<sup>11</sup> were applied. But all gave negative results. The presence of magnesium was confirmed by spectrographic method and its concentration was found to be around 0.05 to 0.1 %. Iron and aluminium were separated by double precipitation with ammonium chloride and ammonium hydroxide, while calcium was precipitated as oxalate which was redissolved and reprecipitated. The filtrate was concentrated, dried and ignited to remove ammonia and dissolved in hydrochloric acid. From this solution magnesium was precipitated by the addition of sodium hydroxide. This precipitate was dissolved in hydrochloric acid and the titan yellow test was applied which gave positive results, and thus the presence of magnesium was confirmed which could not be confirmed by chromatographic methods.

*Preparation of the Sample.*—About 1 g. of finely powdered coal (72 mesh) was taken in a porcelain tray and placed in a muffle furnace. The tempera-

ture was raised to 450°C. in half an hour and maintained for 30 minutes. Then the temperature was further raised to 775°C. ( $\pm 25^\circ\text{C}.$ ) and kept constant for one hour.<sup>12</sup>

One tenth g. of the ash was taken in a small platinum crucible and 0.4 g. of fusion mixture was mixed with it. The crucible was heated in a muffle furnace till the mass fused, and then the temperature was raised to 1000°C. slowly until it formed a uniform liquid. The temperature was further raised to 1100°C. and was maintained for 30 minutes. The crucible after a little cooling was immersed in hot water contained in a small platinum basin. Concentrated hydrochloric acid (1.5 ml.) and a drop of hydrogen peroxide were added and the basin was heated slowly to boiling. The crucible and the lid were cleaned by means of a rubber-tipped glass rod and the liquid along with the silicacious matter was evaporated to dryness on a water bath. After cooling 1 ml. concentrated hydrochloric acid was added followed by 10 ml. of water and was boiled for 10 minutes. The supernatant liquid was filtered and the residue was washed to whiteness with 10% hydrochloric acid and finally with hot water. The filtrate along with the washings was again evaporated to dryness on a water bath and then the basin was placed in an oven at 110°C. for 1 hour. After cooling, 0.5 ml. of concentrated hydrochloric acid was added and digested on a water bath for 10 minutes, followed by the addition of 10 ml. of water and heated to boiling until the precipitate turned white. The

solution was filtered and the precipitate was washed with 10% hot hydrochloric acid till the paper turned white and then was washed three times with hot distilled water.<sup>3</sup>

For the determination of various metallic ions standard reagents were used. The results were further confirmed by placing on the same chromatogram, a spot of a simple salt of the metal to be identified. It was observed that the  $R_f$  value of the spot of simple salt was always a bit lower than the spot of the same ion in the ash.

*Iron.*—It occurs in large concentrations in coal ash and both in ferric and ferrous states, the latter being in much smaller concentration than the former, and most of it is oxidized to ferric state during the processes of fusion, evaporation and filtration due to aerial oxidation. Even then it has been determined by spraying a chromatogram with potassium ferricyanide which gave deep blue spots with it. The spot of ferric iron has a higher  $R_f$  value than the ferrous iron. Spraying with potassium ferrocyanide gave a

Prussian Blue spot with ferric iron, but after a few minutes a similar spot was also observed at the  $R_f$  value of ferrous iron, which presumably was oxidized to ferric state.

*Aluminium.*—It gave a light blue spot with quinalizarin which turned pinkish on spraying with alkaline hydrogen peroxide. Gallacetophenone gave a yellow spot with it just below the purple spot of calcium, when the chromatogram was exposed to ammonia. Magnesium behaves in a similar way, but the two could be easily distinguished from one another by spraying another chromatogram with 8-hydroxyquinoline and exposing to ammonia. On observing under ultraviolet light, aluminium gave a very bright greenish yellow fluorescence and magnesium a bright green fluorescence. Spraying with rhodizonic acid after exposing the chromatogram to ammonia gave a white spot with aluminium surrounded by an orange background.

*Calcium.*—Tannic acid spray and ammonia exposure gave a greenish spot with it. Spraying

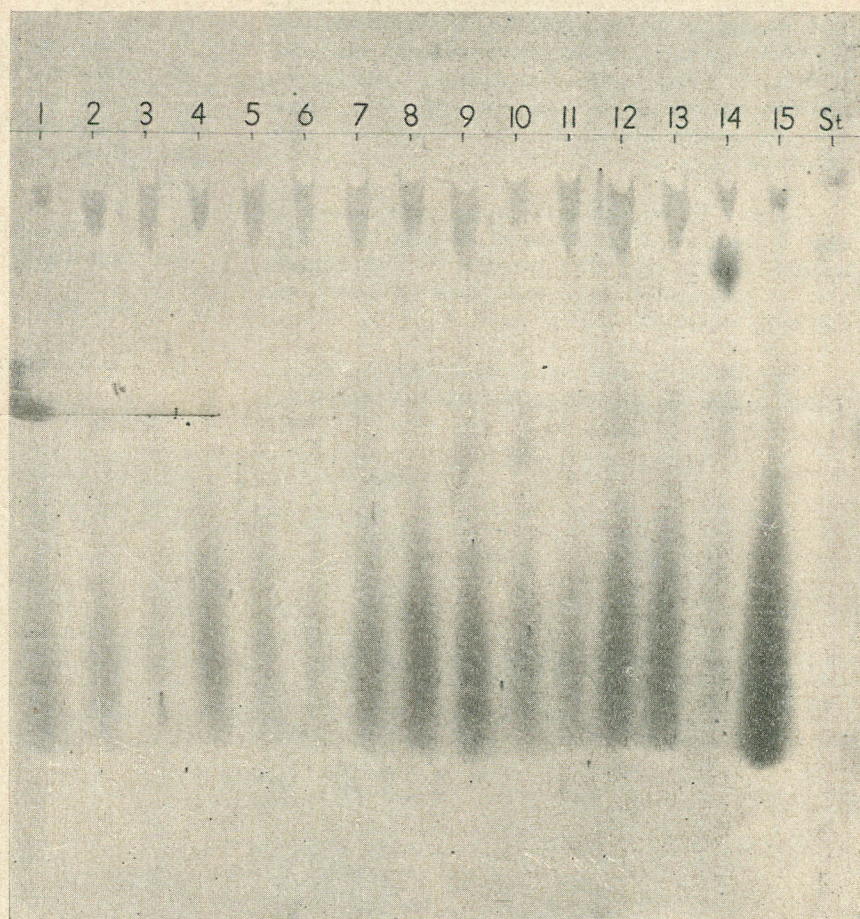


Fig. 3.—Spots of iron developed by spraying potassium ferrocyanide.

with caustic soda after tannic acid as recommended by the McOmie and Pollard<sup>13</sup> was found unsuitable as it produces diffused spots. Gallacetophenone and ammonia gave a purple spot which faded away after 2 or 3 minutes. Exposing the chromatogram to ammonia and spraying rhodizonic acid gave an orange spot which was difficult to distinguish from the background of similar colour.

*Magnesium.*—Its presence in the coal ash could not be confirmed by chromatographic technique. The method for its determination has already been discussed above.

*Lead.*—Rhodizonic acid is the most sensitive reagent for lead. On exposing the chromatogram to ammonia and then spraying it with rhodizonic acid, it gave a violet spot. Treatment with mixed acids (2N hydrochloric and acetic acids 50/50) was found unnecessary as recommended by McOmie and Pollard.<sup>14</sup> Yellow spot is also given with potassium iodide but it is very faint and difficult to distinguish.

*Titanium.*—When the chromatogram is sprayed with potassium ferrocyanide for the determination of iron, the presence of titanium could be observed. It gives a yellow spot. For further confirmation another chromatogram was sprayed with tannic acid containing sodium acetate with which it gave an orange spot.

*Copper.*—In one sample copper was found to exist in such concentrations as to give a definite reddish brown spot with potassium ferrocyanide and a grey green spot with rubeanic acid on exposing to ammonia.

The results of this work are given in Tables 1 and 2, and the spectrographic analysis of coal ash

TABLE 1.—THE  $R_f$  VALUES OF THE VARIOUS CATIONS.

Iron (ferric)	0.58	Titanium	0.18
Iron (ferrous)	0.11	Copper	0.13
Aluminium	0.11	Lead	0.043
Calcium	0.057		

TABLE 2.—THE VARIOUS CATIONS PRESENT IN THE ASH OF DIFFERENT COAL SAMPLES.

1. Abegum	..	Fe (ic), Fe (ous), Al, Ca.
2. Abbotabad	..	Fe (ic), Fe (ous), Al, Ca, Pb, Ti.
3. Chittidand	..	..
4. Chittagong	..	Fe (ic), Fe (ous), Al, Ca.
5. Dalwal	..	Fe (ic), Fe (ous) Al, Ca, Pb, Ti.
6. Diljabba	..	Fe (ic), Fe (ous) Al, Ca, Ti.
7. Jhimpir	..	Fe (ic), Fe (ous), Al, Ca, Ti, Pb.
8. Makerwal (original)	..	..
9. Makerwal (Steam-treated)	..	..
10. Kathar Colliery (Dhok)	..	Fe (ic), Fe (ous), Al, Ca, Pb.
11. Pidh	..	Fe (ic), Fe (ous), Al, Ca, Ti, Pb.
12. Sore Range No. 1	..	..
13. Sore Range Now. 2	..	Fe (ic), Fe (ous), Al, Ca, Ti.
14. Sharigh	..	Fe (ic), Fe (ous) Al, Ca, Ti, Pb, Ca.
15. Slack Khewra	..	Fe (ic), Fe (ous) Al, Ca.

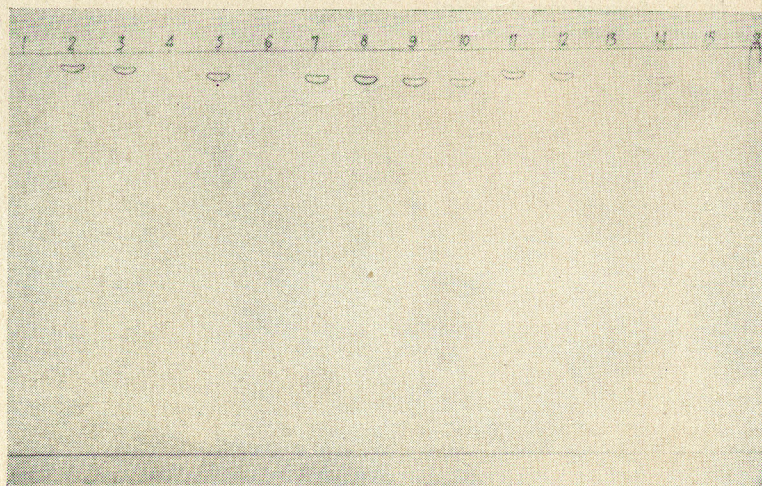


Fig. 4.—Spots of lead developed by spraying rhodizonic acid and 50/50 2N hydrochloric and acetic acids.

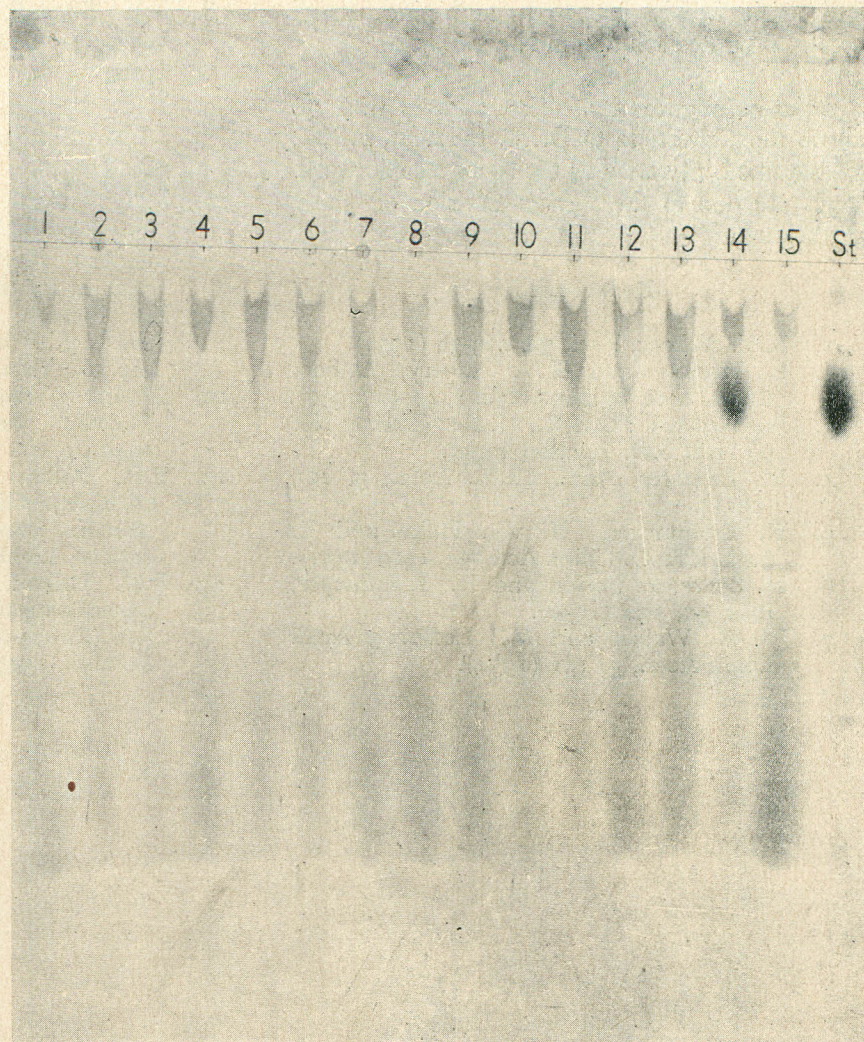


Fig. 5.—Spots of copper developed by spraying rubeanic acid and exposing to ammonia.

TABLE 3.—SPECTRAL LINES OBTAINED IN THE SPECTROGRAPHIC ANALYSIS OF MAKERWAL (ORIGINAL) ASH.

Titanium		Lead	
3349.035	A°	2614.178	A°
3361.213	..	2833.069	..
3372.800	..	3639.580	..
3635.463	..	4057.820	..
3642.675	..		
3653.496	..		

which was carried out on Makerwal sample as a confirmatory test is given in Table 3.

#### Conclusion

From the above account it is clear that this method could very well be applied for the analysis

of other mineral matters. For the estimation of magnesium this method did not prove suitable. Further work in this direction and for the quantitative estimation of mineral matter in coal is in progress.

#### Reagents

Gallacetophenone : 1% (w/v) in 50% ethanol;  
 8-hydroxyquinoline: 0.5 g. in 100 ml. 60% alcohol;  
 potassium ferrocyanide: 5% aqueous solution;  
 potassium thiocyanate: equal volumes of saturated aqueous potassium thiocyanate and acetone;  
 quinalizarin: 0.02% (w/v) in industrial methylated spirit;  
 rhodizonic acid: 0.1% (w/v) sodium salt freshly prepared in distilled water;  
 rubeanic acid: 0.1% (w/v) in industrial methylated spirit;  
 tannic acid: 0.5 g. tannic acid and 1 g. sodium acetate in 10 ml. of warm 60% industrial methy-

lated spirit freshly prepared; and zinc uranyl acetate: saturated solution in N acetic acid.

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