BS 8855-2:2000

Soil analysis —

Part 2: Method for determination of coal tar-derived phenolic compounds

ICS 13.080.10

Committees responsible for this British Standard

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Association of Consulting Scientists
B G Technology
British Ceramic Research Ltd.
British Society of Soil Science
Environment Agency
Laboratory of the Government Chemist
Ministry of Agriculture, Fisheries and Food
Society of Chemical Industry
Soil Survey and Land Research Centre
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Foreword

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 5 and a back cover.

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1 Scope

This British Standard describes a method for determining the concentration of coal tar-derived phenols, namely catechol, resorcinol, phenol, cresols (ortho-, meta-, para-), xylenols (2,3; 2,4; 2,5; 2,6; 3,4 and 3,5); 2-isopropylphenol, 1-naphthol and 2,3,5 trimethylphenol. It is applicable to all types of soil containing concentrations of phenols in the approximate range 0.02 mg/kg to 10 mg/kg soil. Some performance characteristics of the method are summarized in annex A.

The method is not applicable to the determination of halogenated phenols. The range can be extended by suitable dilution of the extracts as required.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of this British Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. For undated references, the latest edition of the publication referred to applies.

BS 7755-3.1, *Soil quality — Part 3: Chemical methods — Section 3.1: Determination of dry matter and water content on a mass basis by a gravimetric method.*

BS 7755-3.5, *Soil quality — Part 3: Chemical methods — Section 3.5: Pretreatment of samples for physico-chemical analyses.*

BS EN ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

3 Principle

A sample of "as-received" soil is extracted with a 60:40 *v/v* methanol:water mixture. Reversed phase high-performance liquid chromatography (HPLC) with direct aqueous injection of the sample, and electrochemical detection, is used to determine the phenolic compound content.

4 Safety precautions

Phenols are both toxic and corrosive and require handling with care. Methanol is toxic and sodium hydroxide is corrosive. Latex or nitrile gloves and eye protection should be worn at all times. Spills should immediately be wiped up with adsorbent tissue and placed in sealed containers used for the disposal of toxic chemicals. Samples should be treated as toxic and harmful.

5 Reagents

5.1 *Citric acid*, (HPLC grade for electrochemical detection).

5.2 *Sodium acetate*, (HPLC grade for electrochemical detection).

5.3 *Sodium hydroxide*, (HPLC grade for electrochemical detection).

5.4 *Methanol*, (HPLC grade for electrochemical detection).

5.5 *De-ionized or distilled water*, of at least Grade 1 as defined in BS EN ISO 3696.

5.6 *Helium*, (chromatography grade).

5.7 *Phenol*, (analytical grade).

5.8 *o-*, *m-*, *p-cresols*, (analytical grade).

5.9 *3,4; 3,5; 2,5; 2,3; 2,4; 2,6 xylenols*, (analytical grade).

5.10 *2-iso-propylphenol*, (analytical grade).

5.11 *Catechol*, (analytical grade).

5.12 *Resorcinol*, (analytical grade).

5.13 *2,3,5-trimethylphenol*, (analytical grade).

5.14 *1-naphthol*, (analytical grade).

6 Apparatus

6.1 *An HPLC system*[1)], capable of delivering an isocratic mobile phase at a rate of 1.0 ml/min, and fitted with an electrochemical detector (see **9.2** for set-up details). (Multiple pumping systems may be used if desired.)

6.2 *A 5µm octadecyl silica (ODS), 25 cm × 4.5 mm internal diameter column (or equivalent)*[1)], fitted with a matching guard column.

6.3 *An injection system*[1)], either manual or automatic capable of injecting up to 100 µl of sample.

6.4 *Glass syringe*, for example 5 ml capacity is suitable.

6.5 *Syringe filters*, nylon, 0.45 µm nominal pore size.

6.6 *Glass fibre filters*, 0.45 µm nominal pore size.

6.7 *Balance*, capable of weighing to an accuracy of not less than $\pm$0.000 1 g.

[1)] For information on suitable equipment contact BSI Information Centre, British Standards House, 389 Chiswick High Road, London W4 4AL.

7 Preparation of reagents and standards

7.1 Stock solutions

7.1.1 *Solvent*

Prepare a 60:40 methanol:water mixture by adding 150 ml ± 1.0 ml of methanol (**5.4**) to 100 ml ± 1.0 ml of distilled or de-ionized water (**5.5**).

7.1.2 *Stock solutions of phenolic compounds*

Weigh accurately 80 mg of each of the phenolic compounds (**5.7** to **5.14**) and quantitatively transfer into the same, or separate 100 ml volumetric flasks, dissolving them in methanol:water (**7.1.1**), to give individual or mixed stock solutions. The concentration of each component is nominally 800 mg/l. Divide the stock solution(s) into 5 ml bottles with tight caps and store at −18 °C.

7.2 Standard solutions for calibration

Prepare standard solutions for calibration from the stock solutions prepared in accordance with **7.1.2**.

For the range 0.3 mg/l to 3.2 mg/l, dilute 0.1, 0.2, 0.3, 0.5, 0.7 and 1.0 ml (±2 % of the respective volume) of the stock solution in 250 ml volumetric flasks with methanol:water (**7.1.1**) to provide calibration standards containing, respectively, 0.3, 0.6, 0.9, 1.5, 2.1 and 3.2 mg/l (±2 % of the respective mass) phenol. The linear range may be extended above 3.2 mg/l if required. Appropriate detector settings are shown in Table 1.

For the range 16 μg/l to 800 μg/l prepare an intermediate working standard solution by diluting 2.5 ml ± 0.05 ml of the stock solution (**7.1.2**) to 100 ml in a volumetric flask with methanol:water (**7.1.1**). Further dilute, 0.2, 0.7, 1.0, 3.0, 5.0 and 10.0 ml (±2 % of the respective volume) in 250 ml volumetric flasks with methanol:water (**7.1.1**) to provide calibration standards, containing respectively 16, 56, 80, 240, 400 and 800 μg/l (±2 % of the respective mass) phenol.

7.3 Blank determinations

Use de-ionized or distilled water (**5.5**) for blank determinations.

7.4 Preparation of the mobile phase

Dissolve 12.2 g ± 0.1 g of citric acid (**5.1**), 4.4 g ± 0.1 g of sodium acetate (**5.2**) and 3.9 g ± 0.1 g of sodium hydroxide (**5.3**) in 1 000 ml ± 5 ml of water (**5.5**) and mix the solution with methanol in the ratio 40:60. Filter through a 0.45 μm glass-fibre filter (**6.6**) and de-gas with helium (**5.6**) for 30 min before use.

Ensure that the mobile phase is at ambient temperature before use (the heats of mixing and dissolution will raise its temperature).

8 Preparation of laboratory sample

If a bulk sample has been submitted to the laboratory, prepare a laboratory sample using an appropriate procedure, for example that given in BS 7755-3.5. Place 150 ml ± 5.0 ml of methanol:water (**7.1.1**) in a screw-topped glass bottle, weigh it and record the mass in grams (M_1). Weigh out between 50 g and 100 g of the bulk sample and add it to the bottle. Reweigh the bottle and record the mass in grams (M_2). Calculate the mass of the laboratory sample (M_s) in grams from the following equation[2)]:

$$M_s = M_2 - M_1$$

Store the sample in the dark at 4 °C and only remove it from this environment immediately prior to analysis.

Before analysis, place the bottle onto a flask shaker for 30 min ± 5 min to extract the phenolic compounds from the sample.

9 Procedure

9.1 Sample for analysis

Using a clean glass syringe (**6.4**) withdraw an amount of the methanol:water extract appropriate to the size of the autosampler vial, from the bottle containing the laboratory sample. Filter through a 0.45 μm nylon syringe filter (**6.5**) into an auto-sample vial. Use polytetrafluoroethylene (PTFE)-faced septa as phenols adsorb onto silicone rubber causing low analytical results.

9.2 Detector

Set the potential on the electrochemical detector to +750 mV, that on the pre-treatment cell to +250 mV and that on the guard cell to +800 mV.

Different detector amplifier ranges shall be used depending on the analyte concentration expected. Analyte concentration ranges over which detector response is expected to be linear, expressed as a function of detector amplifier setting, are given in Table 1.

Table 1 — Analyte concentration ranges giving linear detector response

Detector amplifier setting	Limits of analyte concentration range	
	Lower	Upper
μA	μg/l	mg/l
1	5	0.2
2	10	0.4
5	20	2.0
10	40	4.0
20	80	8.0
50	200	20.0

[2)] As phenols in soil biodegrade, it is common practice for the sample containers to be filled on site to preserve the phenols. Laboratories pre-weigh bottles containing reagent and re-weigh on receipt in the laboratory.

The amplifier range appropriate to the expected analyte concentration shall be selected.

9.3 Chromatograph set-up

Set the total flow rate to 1 ml/min. Use solutions of the individual phenols (e.g. 3.2 mg/l as prepared in **7.2**) to determine the actual retention times of the analytes.

Set the total flow rate to 1 ml/min. Adjust the chromatographic conditions to provide an optimal separation. Inject 100 µl of calibration standards, blanks and samples using either an auto-sampler or manual injection system (**6.3**). Users of manual injection systems shall ensure that identical volumes are injected.

10 Calculations

Areas of the chromatographic peaks are used for quantification. Plot a calibration graph of concentration against peak area and convert sample peak areas into concentration by reading off the graph, or use the appropriate regression line to convert peak areas into concentrations. Calculate the mass of phenolic compounds, P, in the soil sample, in milligrams per kilogram using the following equation:

$$P = P_1 \frac{V}{M_s}$$

where

P_1 is the concentration of phenolic compounds in the methanol:water extract, in milligrams per litre (mg/l);

V is the volume of extract, in litres (l) (volume of methanol:water used in clause **8**);

M_s is the mass of the laboratory soil sample, in kilograms (kg).

If the dry matter content of the soil has also been determined according to BS 7755-3.1, then phenolic concentration may also be adjusted to a dry mass basis.

Indicative retention times are given in Table 2.

Table 2 — Indicative retention times of phenolic compounds

Compound	Retention time min	Ratio of retention time to that of phenol
Resorcinol	3.7	0.63
Catechol	4.3	0.73
Phenol	6.0	1.0
m-cresol	9.0	1.5
p-cresol	9.0	1.51
o-cresol	9.1	1.52
3,4 xylenol	13.4	2.24
2,6 xylenol	13.8	2.3
3,5 xylenol	14.2	2.38
2,3 xylenol	14.3	2.4
2,5 xylenol	14.9	2.49
2,4 xylenol	15.3	2.57
1-naphthol	19.5	3.27
2-isopropylphenol	24.3	4.07
2,3,5-trimethylphenol	24.6	4.12

Annex A (informative)

Performance characteristics

Inter-laboratory trials were organized to test the method given in this British Standard. In these trials the concentrations of phenol, groups of phenolic compounds and the sum of the phenolic compounds determined was measured by a number of laboratories on a number of soils. The soils were obtained from sites formerly used for the manufacture of gas from coal and therefore contained significant quantities of phenolic compounds.

The repeatability (r) and the reproducibility (R) of the results of these analyses are given in Tables A.1 and A.2, respectively.

These values have been calculated based on the method in BS ISO 5725-2:1994.

Table A.1 — Repeatability

Phenolic compound	Number of replicates	Mean concentration mg/kg	Standard deviation (s_r) mg/kg	Repeatability limit (r) mg/kg
Phenol	11	1.2	0.06	0.17
Cresols	11	1.5	0.1	0.28
Xylenols	11	1.6	0.15	0.42
Total	11	5.5	0.55	1.5
NOTE Repeatability limit, $r = 2.8s_r$.				

Table A.2 — Reproducibility

Phenolic compound	Number of laboratories	Mean concentration mg/kg	Standard deviation (S_R) mg/kg	Reproducibility limit (R) mg/kg
Total	18	20.8	2.2	6.2
Total	20	298	48	135
Total	21	16.7	2.7	7.7
Total	27	6.5	1.8	5
Phenol	16	141	17	48
Phenol	20	9	1.4	3.8
Cresols	14	7.3	0.6	1.6
Xylenols	16	3.2	0.5	1.4

NOTE 1 Reproducibility limit $R = 2.8S_R$.
NOTE 2 Total phenols in this table is related to the sum of the phenols analysed, and is not necessarily a measure of the total phenols in the sample.
NOTE 3 Performance data are quoted for the summed cresols and xylenols, rather than the individual compounds, as this was the reporting requirement of BG Properties, who administered a proficiency testing scheme from which the information was obtained.

Bibliography

Standards publication

BS ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method.*

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