
**Solid mineral fuels — Major and minor
elements in hard coal ash and coke
ash — Wavelength dispersive X-ray
fluorescence spectrometric method**

*Combustibles minéraux solides — Éléments en minorité et en majorité
dans les cendres de houille et de coke — Méthode spectrométrique par
fluorescence aux rayons X à une longueur d'onde dispersive*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

- an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;
- an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

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An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 13605 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

Solid mineral fuels — Major and minor elements in hard coal ash and coke ash — Wavelength dispersive X-ray fluorescence spectrometric method

WARNING — Use of this Technical Specification can involve hazardous materials, operations and equipment. This Technical Specification does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this Technical Specification to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This Technical Specification sets out a wavelength dispersive X-ray fluorescence (XRF) procedure for the determination of silicon, aluminium, iron, calcium, magnesium, sodium, potassium, titanium, manganese, phosphorus and sulfur.

The method is applicable to coal ashes, coke ashes and boiler ashes having components within the concentration ranges specified in Table 1.

Table 1 — Ranges of application of the method

Oxide	Concentration range %
SiO ₂	5–100
Al ₂ O ₃	5–80
Fe ₂ O ₃	0,1–25
CaO	0,05–25
MgO	0,05–25
Na ₂ O	0,05–5
K ₂ O	0,05–5
TiO ₂	0,05–5
Mn ₃ O ₄	0,005–5
P ₂ O ₅	0,01–5
SO ₃	0,05–10

NOTE 1 Additional analytes may be included in the method, provided that appropriate validation using reference materials is carried out.

NOTE 2 The precision statistics can be determined using suitable reference materials.

NOTE 3 The method described in this Technical Specification has been tested for the following additional analytes: BaO (0,01 % to 1 %); SrO (0,01 % to 1 %) and ZnO (0,005 % to 1 %).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1171, *Solid mineral fuels — Determination of ash*

ISO 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

ISO 13909-6, *Hard coal and coke — Mechanical sampling — Part 6: Coke — Preparation of test samples*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 apply.

4 Principle

The specimen on which X-ray fluorescence measurements are made is prepared by incorporating the test portion of the sample, via fusion, into a borate glass disc using a casting or press-quenching procedure. By using such a specimen, particle size effects are eliminated.

Calibration is carried out using pure chemicals and/or reference standards, and by making matrix corrections for inter-element effects.

It is expected that laboratories using this Technical Specification have experience in analysing coal ashes of certain compositions and that they employ calibrations that cover these compositions.

5 Reagents

5.1 General

Unless otherwise specified, all reagents shall be of analytical grade and only distilled water or water of equivalent purity shall be used.

5.2 Flux and heavy absorber

Borate fluxes of differing compositions have been found suitable for preparing glass discs from coal/coke ash samples. These fluxes are based on mixtures of one or more of the following: lithium tetraborate, lithium metaborate and lanthanum oxide. Flux may be purchased commercially or prepared by fusion of a mixture of individual reagents.

NOTE The levels of contamination in the flux should be checked. Because levels of contamination may vary from batch to batch, the same batch of flux should be used for all specimens (synthetic standards, external standards and unknowns). When using a fresh batch of flux, reference material specimens should be prepared to determine whether adjustments to the calibration are required.

6 Apparatus

6.1 General

All apparatus shall be constructed from materials that are thermally stable and chemically inert under the conditions of the procedure.

6.2 Crucible

The crucible shall be made from a non-wetting platinum alloy. The crucible shall have sufficient capacity to hold the flux and sample required for fusion. Normally, 15 ml crucibles are adequate for discs of 32 mm in diameter, and 25 ml crucibles for discs of 40 mm in diameter.

NOTE Either platinum/gold or platinum/gold/rhodium alloys are suitable.

Because the crucible and lid (if used) are to be used for fusion work, the normal precautions associated with the care of hot platinum ware should be observed. It is necessary, therefore, to have suitable tongs and a surface on which to rest the crucible. The hot crucible can be rested on a refractory surface, which shall be kept very clean.

Although the crucible is fabricated from an alloy that is not wetted by the glass, for the greatest precision, the crucible should be cleaned between each fusion. The use of citric acid (mass concentration of 20 %), dilute hydrochloric acid (volume fraction of 10 %–50 %) or dilute chlorine-free nitric acid (volume fraction of 10 %) have proven to be suitable for crucible cleaning. The use of an ultrasonic bath will accelerate this process. An alternative method of cleaning is to fuse several grams of flux in the crucible, moving the melt around so as to clean the entire inner surface. The molten flux is poured from the crucible. If a droplet adheres to the crucible, this can easily be flaked off when the crucible is cold.

6.3 Mould

The mould shall be made from non-wetting material. For example, platinum alloy is commonly used for casting discs, and aluminium or graphite is suitable for press quenching.

In the casting technique, the bottom of the disc is the analytical surface. The mould should therefore be flat and sufficiently thick that it is not easily deformed. Casting moulds should be checked regularly for flatness and should be polished regularly, to ensure that the disc releases from the mould. Platens for press-quenching are constructed so that the depth gradually increases from the perimeter to the centre. The analytical surface for press-quenched discs is the surface which contacts the plunger head. Care should be taken not to choose the platen side for intensity measurements.

6.4 Crucible tongs

The crucible tongs shall be platinum-tipped or stainless steel or titanium.

NOTE Stainless steel or titanium tongs are a suitable alternative to platinum-tipped tongs.

6.5 Desiccator

The desiccator shall contain freshly regenerated, self-indicating silica gel.

6.6 Sample holders

Sample holders shall be used for specimen presentation.

6.7 X-ray fluorescence spectrometer

Any conventional wavelength dispersive (sequential, simultaneous, or combination simultaneous/sequential) vacuum path X-ray fluorescence spectrometer may be used, provided that it conforms to precision requirements at the 0,1 % (10^6 counts) precision level.

7 Sample

7.1 Coal and coke ash prepared in the laboratory

The coal or coke sample shall be the analysis sample, prepared to a nominal top size of 212 μm . Sample preparation shall be in accordance with ISO 13909-4 for coal samples or ISO 13909-6 for coke samples.

The sample shall then be ashed using the procedure specified in ISO 1171.

7.2 Coal and coke ash

Coal or coke ash received at the laboratory shall be heated at 815 $^{\circ}\text{C}$ for 15 min and cooled in a desiccator over freshly regenerated, self-indicating silica gel immediately prior to weighing for analysis.

Boiler ash received at the laboratory should be ground to a nominal top size of 63 μm and dried at 105 $^{\circ}\text{C}$ for 1 h, then stored in a desiccator over freshly regenerated, self-indicating silica gel.

8 Procedure

8.1 Number of determinations

Discs shall be prepared and analysed as single determinations and a reference material shall be prepared and analysed at the beginning and end of each batch of samples containing a maximum of 25 samples.

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8.2 Test portion

The mass of the test portion shall be appropriate for the mould size and sample flux ratio chosen.

NOTE 1 Typically, sample-to-flux ratios are in the range 1:5 to 1:10.
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NOTE 2 Typical total mass (sample plus flux) is 4 g for a 32 mm diameter and 7,5 g for a 40 mm diameter mould.

8.3 Check test

At least one reference material of similar composition to the samples being analysed shall be included with each batch of test samples and shall be analysed in parallel with, and under the same conditions as, the test samples. The results for the batch of samples shall be rejected if the results for the reference material fail to meet the acceptance criteria detailed in Annex A.

8.4 Calibration

Calibration shall be effected using either reference materials, synthetic standards or mixtures of reference materials and synthetic standards. Reference materials shall be pre-treated in accordance with the instructions contained on their certificates. If synthetic standards are used, stoichiometric chemicals of appropriate purity shall be used. Chemicals of 99,99 % or higher purity are recommended. Pure chemicals shall be appropriately pre-treated, immediately prior to weighing to ensure stoichiometry and freedom from moisture. Calibration discs shall be prepared in accordance with 8.5.

NOTE Reagents suitable for the preparation of synthetic calibration standards and their appropriate pre-treatment conditions are listed in Annex B.

8.5 Preparation of the fused discs

8.5.1 General

A number of different fluxes and sample-to-flux ratios have proven suitable for the preparation of fused discs that are acceptable for XRF analysis of samples of coal or coke ash. Any consistent combination of sample mass, flux mass and flux type may be used to prepare the fused discs, provided that

- a) disc preparation quality conforms to the requirements of Annex C, and
- b) the precision and accuracy of reference materials prepared using this sample flux combination conforms to the requirements of Annex A.

Discs may be prepared by the casting or press-quenching technique. Both methods will produce glass discs of adequate quality. If the casting technique is used, the sample may be fused with the flux in a crucible and then poured into a separate mould; if an appropriately shaped crucible is used, the fusion may be carried out and the glass allowed to cool in the same crucible.

A conventional electric furnace, high-frequency furnace, or gas burner may be used for heating.

Disc-making machines are available commercially, and these may be used to fuse and cast the discs.

Prior to storage, discs shall be inspected visually, paying particular attention to the analytical surface. The discs shall not contain undissolved material, and shall be whole and free from crystallization and bubbles. Defective discs shall be re-fused or discarded and substitute discs prepared.

Laboratory-prepared ashes for XRF analysis should be freshly prepared; if not, it will be necessary to reheat these to the ashing temperature and hold for 15 min at this temperature prior to preparation of the XRF disc.

Fluxes are in general hygroscopic and hence shall be dried prior to use, or a loss on fusion (LOF) determination shall be carried out and the mass of flux used corrected to an anhydrous basis. Since it is difficult to maintain flux in an anhydrous state, it is recommended that, for work requiring high accuracy, the latter practice be adopted. There is no requirement for determining LOF if the XRF instrument uses loss-eliminated alphas (see de Jongh, 1979).

It is necessary to determine the LOF for boiler ash samples. This is done by allowing the fused material to cool (in a covered crucible) prior to pouring into the mould and reweighing the cooled crucible and fused contents. LOF is equal to the mass of the crucible and its contents prior to fusion minus the mass of the crucible and its contents after fusion. After weighing, the crucible contents is remelted and swirled (to ensure homogeneity), then cast or press-quenched in the normal manner. If loss-eliminated alphas are used, then LOF need not be determined.

NOTE Loss of sulfur can occur at the high temperatures (>1 050 °C) used in the preparation of fused discs.

8.5.2 Disc storage

As soon as possible after preparation, the discs shall be transferred to a desiccator so that adsorption of moisture and the possibility of contamination are minimized.

To avoid contamination of the analytical surface, discs shall be handled by their edges. Care shall be exercised to avoid touching the analytical surface with hands or fingers.

8.5.3 Fused disc quality

The quality of disc preparation shall be checked in accordance with Annex C, as follows:

- a) prior to each new operator commencing analysis of test samples;
- b) by each operator annually.

8.6 XRF measurement

8.6.1 Instrumental conditions

Instruments shall first be tested for precision in accordance with the manufacturer’s instructions.

Suggested analytical lines to be used, and conditions of measurement, are given in Table 2.

Measurements shall be made under vacuum, using an appropriate counter and using specimen rotation if available. A single- or dual-anode target X-ray tube may be used. It is recommended that pulse height selection be used, particularly in the case of P K α , where low concentrations are normally being determined.

Measurements are made at the K α line positions, except where there are overlap interferences at the K α positions. Counting times shall be selected so that, for calibration discs at approximately the midpoint of the range of application of the method (Table 1), at least the number of counts shown in Table 2 are accumulated. Using these counting times, the emitted intensity of each disc shall be recorded as its accumulated count.

The crystals listed in Table 2 are only some of those that may be used. In the case of P K α , the Ge(111) crystal is recommended because it does not give second-order wavelengths. If, however, this crystal is unavailable and a PE crystal is used, pulse height selection shall be used and the settings shall be very carefully selected so that the possibility of interference from the second-order wavelength of Ca K $\beta_{1,5}$ is minimized.

Coarse or fine collimators can be used but, where there is the likelihood of line interference, a fine collimator shall be used, e.g. in the determination of manganese using a chromium target X-ray tube. To minimize interference due to line overlaps, a fine collimator should be used for measuring Ti K α .

Where the crystal contributes significantly to the background, it is also advisable to use a fine collimator, e.g. magnesium and sodium determinations using the TIAP crystal.

Primary-beam filters should not be used as a method for reducing the count rate, as they will alter matrix effects. The exception to this is the determination of manganese using a chromium target X-ray tube, where a filter is required for low backgrounds.

The voltage, in kilovolts, should be that recommended by the supplier for the type of X-ray tube being used. The current, in milliamperes, used with the X-ray tube is not critical but shall be selected so that count rates do not exceed the capability of the counting circuits.

The background will generally be lower with a lower voltage, and there is little or no gain in using a voltage greater than 40 kV for the elements being determined. If magnesium is being determined with a TIAP crystal and a rhodium target X-ray tube, the background will drop considerably as the voltage is lowered.

Table 2 — Analytical lines, crystals and recommended number of counts

Suggested line	Example of crystal	Minimum number of counts for mid-range calibration disc
Si K α	PE	2 × 10 ⁵
Al K α	PE	2 × 10 ⁵
Fe K α	LiF (200)	4 × 10 ⁵
Ca K α	LiF (200)	10 ⁵
Mg K α	LSM ^a (TIAP)	10 ⁵
Na K α	LSM ^a (TIAP)	2 × 10 ⁴
K K α	LiF (200)	4 × 10 ⁴
Ti K α	LiF (200)	4 × 10 ⁴
Mn K α	LiF (200)	4 × 10 ⁴
P K α	Ge(111)	4 × 10 ⁴
S K α	Ge(111)	4 × 10 ⁴

^a Layer synthetic multilayer.

8.6.2 Monitor measurements

To compensate for drifts in X-ray tube output intensity, all X-ray measurements shall be made relative to a monitor specimen. Although different monitor specimens could be used for each component, it is most convenient to use a single specimen containing all the components to be measured. The requirements of the monitor specimen are that it is stable, at least for the time necessary to complete all the measurements associated with a batch of samples, and that it gives intensities for the various components that are comparable to, and preferably a little greater than, those of the specimens to be measured.

A suitable monitor may be prepared by fusion of a mixture of pure chemicals and flux.

The frequency of running the monitor will depend on the stability of the instrument, as determined by the use of suitable quality control samples.

9 Calculation

9.1 General

The results for the concentration of the analysed elements (see Table 1) in coal or coke ash shall be calculated from the measured X-ray intensities after correction for instrumental drift, dead time and matrix effects.

9.2 Correction of instrumental drift

The measured X-ray intensities shall be corrected for instrumental drift using the following equation:

$$N = \frac{N_0 \cdot M^*}{M} \quad (1)$$

where

N_0 is the uncorrected (measured) count;

N is the count after drift correction;

M^* is the count on the monitor disc at the start of the measuring bracket;

M is the count on the monitor disc at the end of the measuring bracket.

9.3 Correction for dead time losses

The drift-corrected X-ray intensities shall be corrected for counting losses arising from the dead time of the counting equipment using the following equation:

$$N_c = \frac{N}{T - N \cdot t} \quad (2)$$

where

N is the counts (after drift correction, using the monitor specimen) accumulated in T seconds;

T is the time, in seconds, in which counts were accumulated;

t is the dead time, in seconds;

N_c is the corrected counts.

NOTE Automatic dead time correction is acceptable, provided that it is correctly adjusted.