Direct Atomic Spectrometric Analysis by Slurry Atomisation

Part 4.* Determination of Selenium in Coal by Electrothermal Atomisation Atomic Absorption Spectrometry†

Les Ebdon and Huw G. M. Parry
Department of Environmental Sciences, Plymouth Polytechnic, Drake Circus, Plymouth, Devon PL4 8AA, UK

The determination of selenium in whole powdered coal without sample dissolution is described. The sample was introduced into a graphite furnace as a slurry for analysis by atomic absorption spectrometry. The coal was slurried in nickel nitrate (matrix modifier), nitric acid and ethanol (wetting agent). The effects of the type of background correction (continuum source or Smith - Hieftje), the furnace programme, the various matrix modifiers and air ashing, particularly on a spectral interference from iron, were investigated. Method calibration was achieved using aqueous standards and sample destruction was carried out *in situ* in the furnace. The preferred method used Smith - Hieftje background correction, the 196.0-nm resonance line and *in situ* air ashing. Selenium was successfully determined in four certified reference material coals with a typical relative standard deviation of 5% at the 1 $\mu g\ g^{-1}$ level. The limit of detection (2σ) of the method is 0.05 $\mu g\ g^{-1}$.

Keywords: *Selenium determination; coal analysis; electrothermal atomisation; atomic absorption spectrometry; slurry atomisation*

The importance of selenium within the environment, its occurrence, distribution, toxicity and the essential levels required by both man and animals, and the analytical methodology for the element have been reviewed.[1,2] The burning of fossil fuels can introduce selenium into the biosphere. Additionally, as selenium can act as a catalytic inhibitor, information on the selenium levels present in the coal used in conversion processes is important. The available techniques for selenium determination include atomic absorption spectrometry (AAS), atomic emission spectrometry, atomic and molecular fluorescence spectrometry, neutron activation analysis and chromatography. Hydride generation may be employed to enhance the sensitivity of the above methods. Comparative studies[3] have indicated that AAS is an attractive choice for the determination of selenium. The best sensitivity and detection limits for the determination of Se by AAS are currently attained by using electrothermal atomisation (ETA). Although this is a sensitive technique, it may be affected by spectral interferences, analyte volatilisation problems and vapour phase interferences.[4] In the determination of selenium, the need for matrix modification is imperative in order to minimise the loss of the analyte during the ashing stage as reported by several workers.[5–12] Manning[13] found spectral interference from iron when selenium was determined at 196.0 nm, the primary resonance line, using continuum-source background correction. This interference was apparently more pronounced at the 204.0-nm line. Coal contains large amounts of iron and only small amounts of selenium. Thus although ETA-AAS is expected to provide the necessary sensitivity, spectral interference may be expected when using continuum-source background correction.

The volatility of selenium creates further problems in its analytical determination. Losses of the element may be encountered in conventional ashing and digestion procedures.[14] Coal is a particularly difficult matrix to digest and most digestion procedures involve elevated temperatures for lengthy periods. Although bomb digestions in a microwave oven may prove to be more rapid and less prone to losses, there may still be potential hazards and occasional losses. To overcome the problems of coal digestion in the determination of volatile elements and to enhance laboratory efficiency by a more rapid analysis, the determination of such elements in coal, using slurries of powdered whole coal, introduced directly into furnaces or plasmas has been advocated.[15–18] In this paper the determination of selenium in coal by slurry introduction - ETA-AAS is described. The performances of the continuum-source and Smith - Hieftje background correction systems, which can eliminate certain spectral interferences, were compared. Sample pre-treatment was kept to a minimum and increased sample destruction was achieved by using air during the ashing stage. The effects of various matrix modifiers were also investigated. The method was calibrated using aqueous standards and validated using certified reference material coals.

Experimental

An Instrumentation Laboratory Video 12 atomic absorption spectrometer fitted with an IL655 graphite furnace (Thermo-Electron, Warrington, UK) was used throughout for the determination of selenium. A selenium hollow-cathode lamp operated at 2.5 mA was used as the primary source of radiation. A spectral band pass of 2 nm was selected to isolate the 196.0-nm line. Either Smith - Hieftje or deuterium arc background correction were employed throughout. Both pyrolytically coated and uncoated tubes and pyrolytically coated micro-boats were used. The optimum furnace conditions found for the determination of selenium in the coal slurry are summarised in Table 1. Slurry samples were injected into the graphite furnace using precision micropipettes (Gilson Pipetteman P, Anachem, Luton, UK).

Chemicals and Reagents

Five certified reference material coals were analysed: bituminous coal [NBS SRM 1632(a) National Bureau of Standards, Washington, DC, USA], sub-bituminous coal (NBS SRM 1635), gas coal (BCR, No. 180, Community Bureau of Reference, Brussels, Belgium), coking coal (BCR No. 181) and steam coal (BCR No. 182).

* For Part 3 of this series see reference 18.
† This paper is dedicated to the memory of Professor John M. Ottaway, a true friend and inspiring mentor.

Table 1. Spectrometer and furnace operating parameters

Furnace programme using pyrolytically coated delayed atomisation cuvettes—

Parameter	Dry		Ash		Atomise	
Time/s	30	40	30	45	5	5
Temperature/°C	80	120	600	800	2200	2350
Gas	Air	Air	Air	N_2	N_2	N_2
Flow-rate/l min^{-1}	7.0	7.0	7.0	2.5	2.5	2.5

Spectrometer parameters using Smith - Heiftje background correction—

Wavelength/nm	196.0
Lamp/mA	2.5
Band pass/nm	2

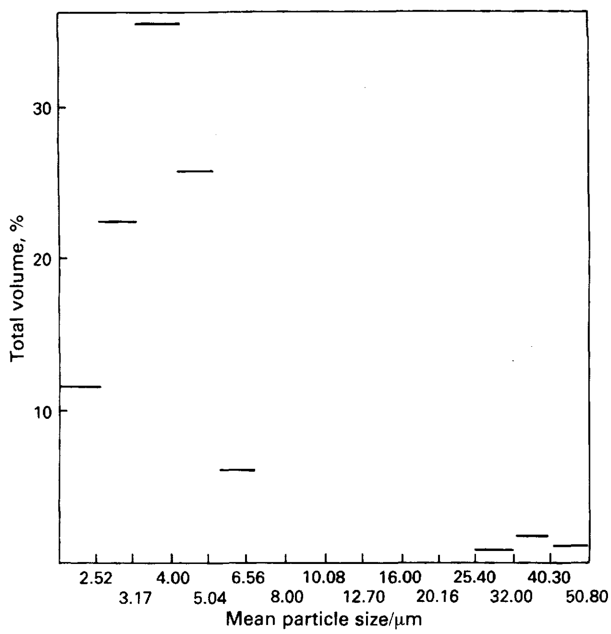

Fig. 1. Particle size distribution, by volume, of coal, NBS SRM 1632(a), after 30 min grinding in a micronising mill

All reagents used were of analytical-reagent grade (AnalaR, BDH Chemicals, Poole, Dorset, UK) and all solutions were prepared with doubly distilled, de-ionised water.

Stock standard solutions

Stock selenium solution (1000 mg l^{-1}) was prepared by the addition of selenium metal (1.000 g) to nitric acid (25 ml) with heating until dissolution was complete. After dilution to 1 l with water, the solution was stored in acid-washed polyethylene bottles.

Working standards were prepared by taking various aliquots of the standard stock solution and diluting with the slurry reagent solution. Suitable precautions were taken when handling the standards, given the known toxicity of selenium.

Sample preparation

Coal was ground with a McCrone micronising mill (McCrone RA, London, UK) for 15–30 min in order to reduce the particle size. Particle size measurements were made with a Coulter Counter TAII (Coulter Electronics, Luton, Bedfordshire, UK), using the electrical zone sensing method. A typical particle size distribution is shown in Fig. 1.

The ground coal (0.4–2.0 g) was weighed accurately into a 50-ml polypropylene screw-cap bottle, to which 10 ml of slurry reagent [containing 10 g l^{-1} of $Ni(NO_3)_2.6H_2O$, 10 g l^{-1} of $Mg(NO_3)_2.6H_2O$, 5 ml l^{-1} of concentrated nitric acid and 100 ml l^{-1} of ethanol] were added. A magnetic stirrer bar was inserted and the bottle sealed and stirred until the coal slurry was homogeneous (typically 5 min). Aliquots of this slurry (10–30 µl) were taken, using a micropipette, whilst stirring continuously and introduced into the graphite furnace. In the final stages of this work and in the proposed method the magnesium nitrate was omitted from the slurry reagent solution.

Results and Discussion

Preliminary Experiments

Initial experiments were performed using a deuterium arc background corrector. Using the 196.0-nm line, large positive interferences were observed when analysing coal slurries. This was attributed to the failure of the correction system to correct for the interference of a broadened iron line with the selenium absorption line. Both iron and selenium were atomised simultaneously within the graphite furnace and thus an overestimation of the selenium content in the coal was obtained.

The above experiments, in which nickel nitrate acted as a matrix modifier, were repeated with the Smith - Hieftje background corrector. The results proved unreproducible. Initially a signal resulted, but in subsequent experiments, no signal was evident. Experiments were devised to elucidate the problem of the diminished selenium signal and several variables were considered. Reducing the ashing temperature to minimise the possible loss of volatile selenium during the ashing stage yielded an erratic signal. This was attributed to the smoke formed during the atomisation stage due to incomplete matrix destruction during the ashing stage. The acid concentration of the slurry was altered in order to minimise the possible generation of gaseous hydrogen selenide, but again no signal resulted. The major problem was considered to be the amount of iron (3% *m*/*m*) which was masking the small amount of analyte. Measurement of both the iron and selenium atomisation profiles suggested that both elements were atomised at similar times with the furnace programme used and indeed over a wide range of similar programmes, *e.g.*, increased atomisation temperatures, increased and decreased atomisation temperature ramps.

Other matrix modifiers were examined in the hope of separating the iron and selenium atomisation profiles. Nickel nitrate was replaced by copper nitrate in the reagent and ash - atomise plots constructed using both copper nitrate and nickel nitrate in coated and uncoated tubes. It was evident that the pyrolytically coated tubes with a nickel nitrate modifier were preferable as higher atomisation temperatures could be tolerated. No signal for selenium in coal was observed when a palladium nitrate matrix modifier was used. Having established that nickel nitrate was the preferred modifier, hydrogen peroxide was added to the slurry reagent in the hope that this would produce a more oxidising environment for the ashing stage. No selenium signal was obtained from the coals although various concentrations of hydrogen peroxide together with various furnace conditions were applied.

A series of experiments was devised using selenium solutions, nickel nitrate solutions and iron oxide slurries. As expected a low signal resulted when nickel nitrate was omitted owing to the loss of analyte during the ashing stage. However, the signal was enhanced when the nickel nitrate was included. This was attributed to the formation of nickel selenide which is stable at more elevated temperatures, which is indicative of a successful modification of the analyte. The addition of both nickel nitrate and iron oxide (1% *m/V*) caused the signal to be depressed compared with the selenium plus nickel solution. Omission of nickel nitrate, but inclusion of both the iron and selenium, produced an enhanced signal compared with the pure selenium signal. The conclusion drawn from these experiments was that iron oxide acted as a matrix modifier in the absence of nickel nitrate, but in the presence of both nickel nitrate and iron oxide, the analyte signal was supressed due to spectral interference.

Ash - atomise plots were constructed for a solution of selenium in a slurry of iron oxide particles and compared with similar plots for a solution of selenium in a nickel nitrate solution. It was apparent that a higher temperature was required to atomise the selenium from the iron oxide slurry and that a higher ashing temperature could be tolerated. A third ash - atomise plot was constructed using two slurries of iron oxide, only one of which contained selenium solution. All measurements were made at the selenium 196.0-nm resonance line. It was possible to construct "ash - atomise plots" for both slurries. On comparison of both plots, the apparent atomisation temperature for the pure iron oxide slurry was higher than the atomisation temperature observed using the iron oxide slurry containing selenium. This suggested that with careful control and manipulation of the furnace temperature and ramping of the furnace programme, it might be possible to separate the selenium signal from the iron interference. In practice this was not possible and it is suggested that iron and selenium form a condensed phase selenide which ensures co-evolution of the atoms in mixtures.

Hydrogen sulphide was bubbled through the selenium in iron oxide slurry in an attempt to liberate the selenium from the iron. Various amounts of hydrogen sulphide gas were bubbled through the slurry which was observed to change colour. When attempts were made to construct ash - atomise plots erratic results were obtained. This, together with the unpleasant nature of hydrogen sulphide, caused the termination of this work. Ammonium sulphide solution was also used but with little advantage.

Further experiments were conducted to determine the level of iron (as iron oxide in slurry form) that Smith - Hieftje background correction could tolerate at both the primary and secondary selenium wavelengths (196.0 and 204.0 nm). At the 196.0-nm line addition of iron oxide to 50 ng ml^{-1} selenium solutions caused an initial enhancement of the signal up to 0.8% *m/V* iron oxide in the slurry, thereafter the signal decreased. The experiments were repeated at the less sensitive 204.0-nm wavelength and owing to the lack of sensitivity, the standard selenium concentration was increased to 150 ng ml^{-1}, and various amounts of iron oxide were added. The results indicated that no interference from iron was observed at this wavelength, but unfortunately this line is five times less sensitive and thus problems with coal analysis remain.

Use of Air Ashing

When dry powdered coal was introduced into the graphite furnace on a micro-boat without the addition of any form of matrix modifier, selenium absorption signals were observed. Not all the coals studied produced a signal. By introducing air, from a cylinder, at the ashing stage a selenium signal was obtained from all the coals investigated. A simple procedure was employed using an air cylinder and a nitrogen cylinder connected to the gas supply of the furnace via a two-way switching valve. Using a flow of air during the ashing stage promoted more efficient ashing and markedly reduced the background levels observed in coal analysis (see Figs. 2 and 3). Subsequently attempts were made to convert this solid sampling technique into a slurry analysis procedure, as slurries are simple to handle and can be micropipetted, which is more rapid than the use of a microbalance as required by the boat technique. Additionally, it was intended to develop an aqueous solution calibration which is more suited to slurry analysis. Initially a slurry reagent was used which omitted nickel nitrate as this had seemed to aggravate the iron interferences observed above. Without nickel nitrate in the slurry no signals were obtained and this was attributed to premature loss of the selenium, presumably as hydrogen selenide. When nickel nitrate was added to the slurry usable selenium signals were obtained.

Optimisation Studies

The method was optimised principally by careful study of the ash - atomise curves and the most successful programme is given in Table 1. The most significant advance achieved in the development of the method was considered to have been obtained by using air during the drying and ashing stages. The compressed air was introduced into the furnace gas line via a switching valve. The programme commenced with air flowing through the furnace head and at the end of the ashing stage the gas flow was switched manually to nitrogen. It became apparent that switching from one gas to another was a critical parameter. If air was present during the atomisation stage, a dramatically increased temperature in the furnace tube resulted, which led to rapid tube destruction. To avoid this situation, the nitrogen flow was always introduced before the atomisation cycle commenced. It would be possible to

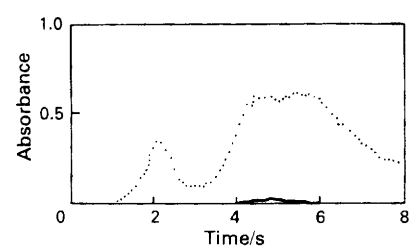

Fig. 2. Atomisation profile for selenium in coal, NBS SRM 1632(a) without air ashing: solid line, selenium signal corrected using Smith - Hieftje background correction; and broken line, total signal indicating high background

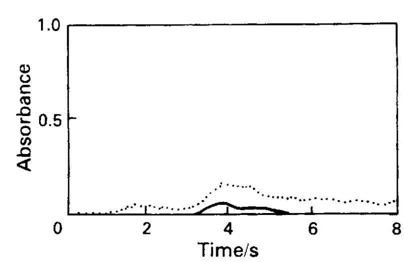

Fig. 3. Atomisation profile for selenium in coal NBS SRM 1632(a) with air ashing: solid line, selenium signal corrected using Smith - Hieftje background correction; and broken line, total signal indicating high background

Table 2. Determination of Se in reference coals (± SD) by direct slurry atomisation using Smith - Hieftje background correction at 196.0 nm

Sample	Proposed slurry method/ $\mu g\, g^{-1}$	Certified value/ $\mu g\, g^{-1}$
NBS SRM 1632(a) . .	2.1 ± 1.2	2.6 ± 0.7
NBS SRM 1635	<0.05	0.9 ± 0.3
BCR No. 180	0.92 ± 0.10	1.32 ± 0.06
BCR No. 181	1.14 ± 0.09	1.15 ± 0.05
BCR No. 182	0.59 ± 0.06	0.68 ± 0.07

automate this switching readily using a pneumatic valve for routine analysis. It is believed that the air ashing confers two benefits. Firstly, the organic matrix of the coal is more readily destroyed thereby lowering the over-all background. Secondly, as the spectral interference is due to iron, which was atomised simultaneously with selenium as an iron selenide appeared to be formed, conversion of the iron species into iron oxide reduces the extent of the interference to a tolerable level for the Smith - Hieftje correction system.

Evaluation of Method

Various amounts of coal were taken (0.5–2.0 g) and suspended with nickel nitrate, ethanol and water. The slurry was agitated to ensure homogeneity before introduction into the furnace. A detection limit (2σ) of 0.05 $\mu g\, g^{-1}$ of selenium in coal was obtained using a 15% *m/V* slurry.

Selenium was determined in five certified reference material coals. The results are given in Table 2. For four of the coals good agreement was obtained with certified values, the exception being NBS SRM 1635, from which no signal was observed. The reason for this was unclear especially as the Se : Fe ratio is similar to that for the other coals. Further work is required to elucidate this problem fully. However, NBS SRM 1635 can be analysed using solid sampling and micro-boats as described above. In the proposed slurry method the furnace cycle time is of the order of 3 min which includes a furnace cool time.

The method offers the advantages of slurry atomisation along with simple calibration using aqueous standards. The relative standard deviation is typically 5% at the 1 $\mu g\, g^{-1}$ level.

Conclusion

Major problems may be encountered in the determination of selenium in coal slurries due to interference from iron. The use of continuum-source background correction or the less sensitive 204.0-nm selenium line did not successfully eliminate the problems. At the 204.0-nm line, there was reduced interference using Smith - Hieftje background correction, but this line did not prove sufficiently sensitive for coal analysis. Attempts to separate temporally the selenium and iron atomisations by means of matrix modification, addition of H_2O_2, H_2S and modification of furnace programmes proved unsuccessful. The introduction of air ashing in conjunction with Smith - Hieftje background correction and a carefully optimised furnace programme allowed the successful determination of selenium in coal slurries. This method offers the well known advantages of slurry atomisation which, in comparison with dissolution techniques, eliminates the lengthy and contamination-prone sample preparation stages, thereby increasing the speed and accuracy of analysis.

The authors acknowledge the support of H.G.M.P. by SERC and British Coal under the CASE Studentship Scheme.

References

1. Raptis, S. E., Kaiser, G., and Tolg, G., *Fresenius. Z. Anal. Chem.*, 1983, **316**, 105.
2. Verlinden, M., Deelstra, H., and Adriaenssens, E., *Talanta*, 1981, **28**, 637.
3. Pierce, F. D., and Brown, H. R., *Anal. Chem.*, 1977, **49**, 1417.
4. Langmyhr, F. J., *Analyst*, 1979, **104**, 993.
5. Ediger, R. D., *At. Absorpt. Newsl.*, 1975, **14**, 127.
6. Alfthan, G., and Kumpalainen, J., *Anal. Chim. Acta*, 1982, **140**, 222.
7. Kirkbright, G. F., Hsiao-Chaun, S., and Snook, R. D., *At. Spectrosc.*, 1980, **1**, 85.
8. Brown, A. A., Ottaway, J. M., and Fell, G. S., *Anal. Proc.*, 1982, **19**, 321.
9. Oster, O., and Preewelz, W., *Clin. Chim. Acta*, 1982, **124**, 277.
10. Carnrick, G. R., Manning, D. C., and Slavin, W., *Analyst*, 1983, **108**, 1297.
11. Saeed, K., Thomassen, Y., and Langmyhr, F. J., *Anal. Chim. Acta*, 1979, **110**, 285.
12. Alexander, J., Saeed, K., and Thomassen, Y., *Anal. Chim. Acta*, 1980, **120**, 377.
13. Manning, D. C., *At. Absorpt. Newsl.*, 1978, **17**, 167.
14. Welz, B., Schlemmer, G., and Völlkopf, U., *Spectrochim. Acta, Part B*, 1984, **39**, 501.
15. Ebdon, L., and Pearce, W. C., *Analyst*, 1982, **107**, 942.
16. Ebdon, L., and Parry, H. G. M., *J. Anal. At. Spectrom.*, 1987, **2**, 131.
17. Ebdon, L., and Wilkinson, J. R., *J. Anal. At. Spectrom.*, 1987, **2**, 39.
18. Ebdon, L., and Wilkinson, J. R., *J. Anal. At. Spectrom.*, 1987, **2**, 325.

Note—Reference 18 is to Part 3 of this series.

Paper J7/90
Received June 23rd, 1987
Accepted September 7th, 1987