# Evaluation of Digestion Procedures for the Determination of Selenium in Soil Comparing Vapour Generation and Graphite Furnace Atomic Absorption Spectrometry With Zeeman-effect Background Correction

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In this work, three mixed acid digestion methods, $HNO_3$ - $HClO_4$ - HF, $HNO_3$ - $H_2O_2$ - HF and $HNO_3$ - HCl - HF, have been studied. The digest solutions were analysed for selenium by graphite furnace atomic absorption spectrometry (GFAAS) using either deuterium or Zeeman-effect background correction systems and by vapour generation atomic absorption spectrometry (VGAAS). Because soil samples contain substantial amounts of iron and phosphorus, the accurate determination of selenium by deuterium arc background corrected GFAAS is complicated by the well documented spectral interferences which give rise to over-correction. However, this over-correction can be simply eliminated by the use of Zeeman-effect background corrected GFAAS. The accuracy of the methods was assessed by the use of the NIST Standard Reference Material (SRM) Coal Fly Ash 1633A. The precision of the measurements (RSD) ranges from 3.8 to 9.9% with Zeeman-effect GFAAS, and from 0.2 to 1.5% with VGAAS, for selenium concentrations of up to 20 ng ml$^{-1}$. The three digestion methods give comparable results on both Zeeman-effect GFAAS and VGAAS. However, the $HNO_3$ - $H_2O_2$ - HF and $HNO_3$ - HCl - HF procedures are preferred because they are simple and less time consuming.

**Keywords:** *Selenium determination; soil; coal fly ash; Zeeman-effect graphite furnace atomic absorption spectrometry; vapour generation atomic absorption spectrometry*

Interest in the determination of selenium has been growing in recent years. Selenium is a trace element in the environment and exists at levels which may be anywhere between essential and toxic to both humans and animals. It is claimed that concentrations of greater than 1 µg g$^{-1}$ of selenium in the daily nutrition leads to selenosis[1]; however, selenium deficiency causes a severe health hazard, especially to livestock and poultry.[2] Hence, there is great concern about the presence of selenium in the environment due to its nutritional importance as well as its reported link with adverse health effects.

Several workers have reported on the use of wet digestion methods for the determination of selenium in soil and coal fly ash samples by atomic absorption spectrometry (AAS).[3-5] In this study, three mixed acid digestion methods, $HNO_3$ - $HClO_4$ - HF, $HNO_3$ - $H_2O_2$ - HF and $HNO_3$ - HCl - HF, were employed and the results of the determination of selenium on both soil and coal fly ash samples by Zeeman-effect graphite furnace AAS (GFAAS) and vapour generation AAS (VGAAS) are presented and compared. In order to demonstrate the accuracy and precision of the methods, a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) Coal Fly Ash 1633A was used.

## Experimental

### Instrumental

A Varian SpectrAA-40 or -400 Zeeman graphite furnace atomic absorption spectrometer with programmable sample dispenser and a Varian SpectrAA-40 or -400 atomic absorption spectrometer equipped with a GTA-96 graphite tube atomiser and deuterium-arc background correction were used. The programmable sample dispenser allows for selected volumes of blank, modifier, standard and sample solution to be taken automatically and introduced into the graphite tube.

A Varian SpectrAA-400 atomic absorption spectrometer was connected with a Varian VGA-76 vapour generation accessory[6] for the hydride generation study. The VGA-76 was operated under the manufacturer's recommended conditions

for Se.[7] Three replicates of 5-s integrations were used for each measurement.

In the graphite furnace work, pyrolytic graphite coated partitioned graphite tubes were used and the inert gas was argon. A SpectrAA selenium hollow-cathode lamp was used under the recommended conditions.

### Reagents

Analytical-reagent grade chemicals and distilled, de-ionised water were used throughout the study.

*Nitric acid.* 70% *m/m*, Univar.

*Hydrochloric acid.* 36% *m/m*, Univar.

*Perchloric acid.* 70% *m/m*, Univar.

*Hydrofluoric acid.* 40% *m/m*, BDH.

*Hydrogen peroxide.* 30% *m/V*, Mallinckrodt.

*Selenium working standard.* A 100 ng ml$^{-1}$ Se$^{IV}$ standard in 0.5% *V/V* HCl was prepared in de-ionised, distilled water for Zeeman GFAAS. Standards of 20 and 50 ng ml$^{-1}$ of Se$^{IV}$ in 1 M HCl were prepared in de-ionised, distilled water for the vapour generation AAS.

*Palladium modifier.* The $PdCl_2$ standard solution was diluted with de-ionised water to give a 500 µg ml$^{-1}$ solution of Pd.

*Programmable sample dispenser rinse solution.* A solution of 0.5% *V/V* HCl and 0.05% *V/V* Triton X-100 was prepared with de-ionised, distilled water and served as the rinse solution for the graphite furnace studies.

### Sample Preparation

A sample of soil was placed in an oven and dried at 45 °C for 48 h, then ground using a mortar and pestle to obtain fine particles. Approximately 0.5 g of a dry soil sample or 0.2 g of coal fly ash was accurately weighed into a clean 250-ml PTFE beaker.

*$HNO_3$ - $HClO_4$ - HF digestion[3]*

A 10-ml volume of $HNO_3$ was added to the sample, any visible reaction was allowed to proceed and subside, then 10 ml of

$HClO_4$ were added. The mixture was heated on a hot-plate until the $HNO_3$ boiled off and white fumes of $HClO_4$ were apparent. Heating was continued until 2–3 ml of $HClO_4$ remained. (If the solution was dark in colour, an extra 10 ml of $HClO_4$ were added to turn it to grey or white.) Then 5 ml of 2% $KMnO_4$ solution were added and the mixture left to stand for 5 min, and a further 5 ml of 2% $K_2S_2O_8$ solution added and heated for about 2 min. A 10-ml volume of HF was added and heating was continued until 2–3 ml of solution remained. The addition of $KMnO_4$ and $K_2S_2O_8$ is to ensure an oxidising environment in which the analyte is in the higher oxidation state, otherwise, volatilisation losses of selenium may result from the addition of HF.[3] (The purple colour of the solution was maintained throughout the heating process by adding an extra amount of $KMnO_4$.) At this stage, most of the solid should have dissolved, if not, another 10 ml of HF should be added. To the dissolved residue, 10 ml of 1 + 1 HCl were added and the mixture heated for 1 min. The solution was transferred into a 100-ml polypropylene calibrated flask and made up to volume.

### $HNO_3$ - $H_2O_2$ - HF digestion

A 5-ml volume of $HNO_3$ was added to the sample and heated for 5 min, 10 ml of $H_2O_2$ were then slowly added dropwise to the mixture and the reaction allowed to proceed. When the reaction subsided the heating was continued on a hot-plate until approximately 2 ml of liquid remained. Then 5 ml of HF were added and heating was continued until again approximately 2 ml of liquid remained. The solution was cooled and transferred into a 100-ml polypropylene calibrated flask and made up to the mark with distilled, de-ionised water.

### $HNO_3$ - HCl - HF digestion[4]

A mixture of 5 ml of aqua regia and 2 ml of HF was added to the sample and heated for 2 h at 100 °C, while covered. After 2 h, 1 g of boric acid was added to the hot digest solution in order to complex the excess of HF. The solution was then transferred into a 100-ml polypropylene calibrated flask and made up to the mark with distilled, de-ionised water.

## Results and Discussion

### Determination of Se by Zeeman-effect GFAAS

The determination of selenium by Zeeman-effect GFAAS was carried out directly on the digested sample solutions. The absorbance measurements were made using peak heights.

### Spectral interferences

In the determination of Se by deuterium-arc background corrected graphite furnace AAS, interferences occur due to large amounts of Fe or P present in the sample.[7,8] In fact, soil and coal fly ash tend to contain large amounts of Fe and small amounts of P. There was approximately 3% Fe and 0.1% P in the soil sample and 9.4% Fe in the NIST SRM Coal Fly Ash, and therefore, inter-element interferences were expected. When a deuterium-arc background correction system was used, these spectral interferences resulted in over-compensation. Large negative peaks interfering with the Se atomic peak were observed as shown in Fig. 1.

These negative peaks occur because the spectral lines of interfering elements cause an over-correction by absorbing radiation from the continuum source. This was confirmed by preparing a solution containing 150 µg $ml^{-1}$ of $Fe^{III}$ (equivalent to that in the soil digest solution) and 20 ng $ml^{-1}$ of $Se^{IV}$, which showed an over-correction when measured using the deuterium-arc background corrected graphite furnace. If Zeeman-effect background correction is used, background correction occurs at the exact analyte wavelength. The use of Zeeman-effect background correction overcomes the problems of Fe and P spectral interferences in the determination of
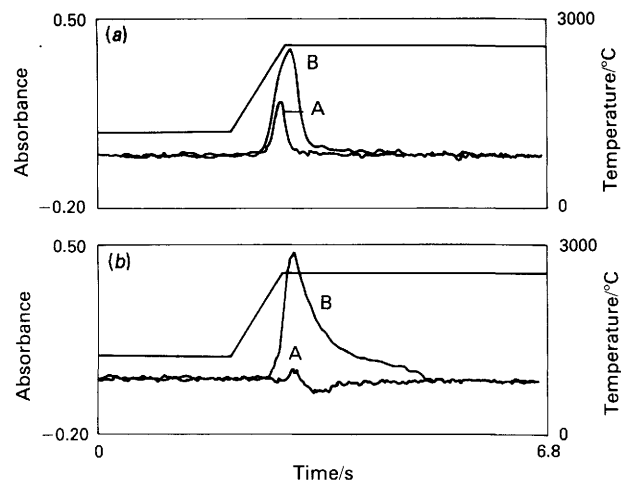


**Fig. 1.** Background correction of soil digest solution at the Se 196.0-nm line of a 40 ng $ml^{-1}$ Se standard addition signal by: (a) Zeeman-effect background correction and (b) deuterium-arc background correction; A, atomic absorption signal and B, background signal

Se as confirmed in Fig. 1. Hence subsequent studies were performed using the Zeeman graphite furnace atomiser.

### Modifier

Investigations on the use of chemical modifiers to improve the thermal stabilisation of Se have been well documented.[9] The use of $Ni(NO_3)_2$ solution seems to be the most popular method, however, with the recent increasing interest in using Pd as a modifier,[10-13] especially with the addition of a reducing agent on the Pd modifier,[14] it has been judged that more consistent performance was obtained with Pd than with Ni. Knowles and Brodie[15] have evaluated the effect of using different modifiers and various amounts of reduced Pd modifier on the determination of Se in blood by Zeeman-effect GFAAS, which resulted in a recommendation to use a solution containing 500 ug $ml^{-1}$ of $PdCl_2$ and 0.25% m/V of ascorbic acid. The function of ascorbic acid was to reduce Pd ions in solution to elemental Pd, and consequently, mixing of ascorbic acid and the Pd solution causes a precipitation of the metal. Therefore, the two solutions are introduced into the graphite tube separately. The Pd modifier was injected first, using the pre-injection facility of the programmable sample dispenser. The ascorbic acid was contained in the blank solution which was then added by the auto-sampler and mixing occurred in the tube.

### Ashing studies

Ashing studies were performed to determine the preferred furnace parameters and also to determine the effectiveness of the Pd - ascorbic acid modifier for the determination of Se. The effect of ashing temperature on a solution of Se with and without the use of a Pd modifier is illustrated in Fig. 2. Without the use of a modifier, the maximum ashing temperature for Se is in the range 400–500 °C, whereas with the Pd - ascorbic acid modifier, a much higher ashing temperature is obtained, with Se remaining thermally stable up to 1200 °C. The maximum ashing temperature of 1200 °C was thus used in this work.

Fig. 3 shows the result of an ashing study on the soil and coal fly ash solutions containing a standard addition of Se and the Pd - ascorbic acid modifier. This confirms that the appropriate ashing temperature for Se is 1200 °C in these samples. The furnace parameters used are listed in Table 1.

### Results

Calibration was achieved with the standard additions method using peak-height measurements and the use of the programmable sample dispenser for the preparation of the
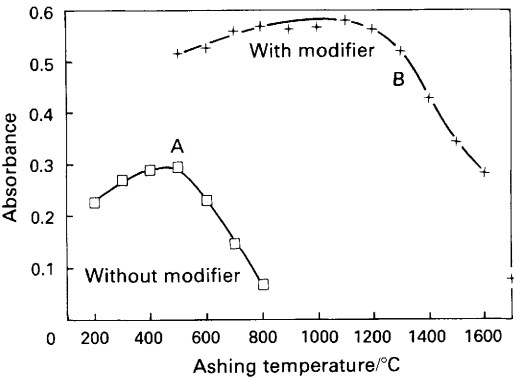
**Fig. 2.** Effect of increasing ashing temperature on: A, 2 ng of Se and B, 2 ng of Se with 5 µg of Pd and 25 µg of ascorbic acid
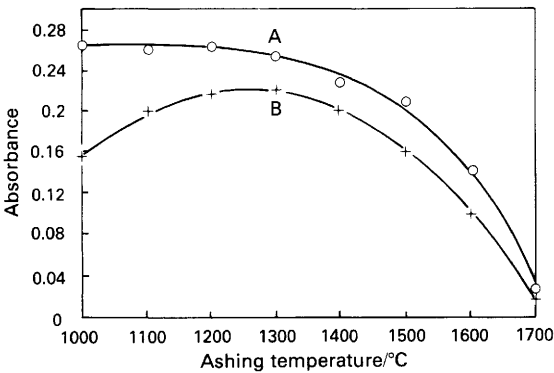


**Fig. 3.** Effect of increasing ashing temperature on 10 µl of: A, soil digest and B, coal fly ash digest (NIST) with 0.5 ng of Se added and 20 µg of Pd and 25 µg of ascorbic acid

additions according to the volumes listed in Table 2. A typical calibration graph for the soil digest is presented in Fig. 4 which also includes error bars indicating the precision of each measurement.

Measurements of precision based on ten replicate analyses of the soil sample gave relative standard deviations ranging from 3.8 to 9.9% for the absorbance readings of a 20 ng ml$^{-1}$ solution of Se.

The results of the analyses by Zeeman-effect GFAAS from triplicate measurements of the samples are listed in Table 3. The results for a soil sample using the three different digestion methods are very similar. To test the accuracy of the methods, the NIST SRM Coal Fly Ash 1633A was analysed and Table 3 shows that the values found compared favourably with the certified value, irrespective of the digestion method.

A typical atomic absorption signal for Se from the NIST coal fly ash is shown in Fig. 5. It is clear that a significant background signal remains even after ashing at 1200 °C, and that the atomic absorption signal is well shaped.

## Determination of Se by Vapour Generation AAS

Because of the different analytical requirements, the determination of Se by vapour generation AAS was carried out after further sample treatment. An aliquot of the digested sample solution was treated with concentrated HCl to obtain the correct acidity for the reduction of Se$^{VI}$ to Se$^{IV}$ prior to measurement of the atomic absorption signals. The optimum acid concentration is between 6 and 7 M HCl.[7] The reduction of the Se is achieved either by heating the solution to 70 °C for 10 min or by allowing it to stand at room temperature for 1 h. In the present work, the solution was heated to 70 °C for 10 min in 6 M HCl and allowed to cool. Calibration was achieved with aqueous standards ranging from 20 to 50 ng ml$^{-1}$ of Se$^{IV}$

**Table 1.** Furnace parameters

| Step No. | Temperature/°C | Time/s | Gas flow/ 1 min$^{-1}$ | Gas type | Read command |
|---|---|---|---|---|---|
| 1 | 85 | 5.0 | 3.0 | Normal | No |
| 2 | 95 | 50.0 | 3.0 | Normal | No |
| 3 | 120 | 10.0 | 3.0 | Normal | No |
| 4 | 1200 | 5.0 | 3.0 | Normal | No |
| 5 | 1200 | 1.0 | 3.0 | Normal | No |
| 6 | 1200 | 2.0 | 0.0 | Normal | No |
| 7 | 2600 | 0.9 | 0.0 | Normal | Yes |
| 8 | 2600 | 2.0 | 0.0 | Normal | Yes |
| 9 | 2600 | 2.0 | 3.0 | Normal | No |

**Table 2.** Furnace sampler parameters: volumes of solutions dispensed (µl)

| Solution | Standard | Sample | Blank | Modifier |
|---|---|---|---|---|
| Blank .. .. .. | — | — | 20 | 10 |
| Standard addition 1 .. | 2 | 10 | 8 | 10 |
| Standard addition 2 .. | 4 | 10 | 6 | 10 |
| Sample .. .. .. | — | 10 | 10 | 10 |

**Table 3.** Results for Zeeman-effect graphite furnace AAS analysis

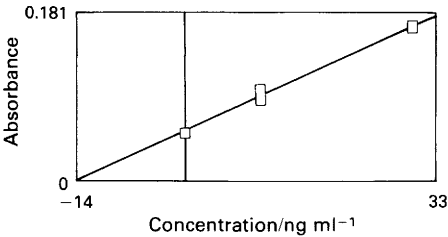| | Se concentration/µg g$^{-1}$ | | |
|---|---|---|---|
| | | NIST SRM Coal Fly Ash 1633A | |
| Digestion method | Soil sample | Found | Certified |
| HNO$_3$ - HClO$_4$ - HF .. .. | 1.2 | 9.9 | 10.3 ± 0.6 |
| HNO$_3$ - H$_2$O$_2$ - HF .. .. | 1.5 | 10.0 | 10.3 ± 0.6 |
| HNO$_3$ - HCl - HF .. .. | 1.4 | 9.7 | 10.3 ± 0.6 |



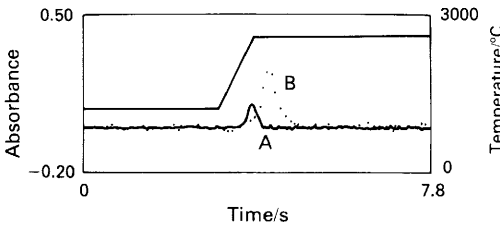**Fig. 4.** Standard additions calibration graph of soil digest



**Fig. 5.** Signal graphics presentation for Se atomic absorption signal with Zeeman-effect background correction together with the furnace temperature profile of coal fly ash digest: A, atomic absorption signal and B, background signal
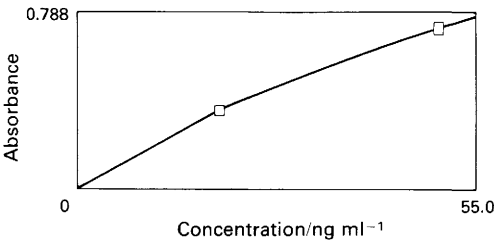


**Fig. 6.** Calibration graph prepared using aqueous Se standards by VGAAS

**Table 4.** Results for vapour generation AAS analysis

| | | | Se concentration/$\mu g\ g^{-1}$ | | |
| --- | --- | --- | --- | --- | --- |
| | | | | NIST SRM Coal Fly Ash 1633A | |
| Digestion method | | | Soil sample | Found | Certified |
| $HNO_3 - HClO_4 - HF$ | .. | .. | 1.1 | 10.7 | $10.3 \pm 0.6$ |
| $HNO_3 - H_2O_2 - HF$ | .. | .. | 1.5 | 9.8 | $10.3 \pm 0.6$ |
| $HNO_3 - HCl - HF$ | .. | .. | 1.6 | 10.7 | $10.3 \pm 0.6$ |

in 1 M HCl. The calibration graph is shown in Fig. 6 which includes error bars indicating the precision of each measurement.

The results of analyses are those for triplicate measurements and are listed in Table 4. The vapour generation AAS results for soil with the three different digestion methods give good agreement and are comparable to the certified NIST value. The precision of the triplicate measurements (RSD) ranges from 0.2 to 1.5% for Se concentrations up to 20 ng ml$^{-1}$.

### Comparison Between Zeeman-effect GFAAS and VGAAS Techniques

The three digestion methods give comparable results for Se using both Zeeman-effect GFAAS and vapour generation AAS techniques for soil and NIST coal fly ash. The accuracy of the methods was confirmed by the good agreement between the found values and the certified values of the NIST standard reference sample. Therefore, both the Zeeman-effect GFAAS and VGAAS techniques are capable of determining Se in soil and coal fly ash by either one of the three sample dissolution methods.

Owing to the potentially hazardous nature of digestion involving the use of perchloric acid[16] and the time required for this procedure, the $HNO_3 - HClO_4 - HF$ digestion method is not considered to be the preferred method. Indeed, many laboratories endeavour to avoid the use of perchloric acid. It has been found that the other acid digestion procedures are simple to use, less time consuming and give essentially the same analytical results.

During this study, it was noted that lower values of Se in the digestion solutions were found after the solutions had been standing for 2–3 d. This may have been due to adsorption of Se on to the container walls. Therefore, it is suggested that the analysis should proceed soon after the sample dissolution is completed.

### Conclusion

Because of the presence of the relatively high amounts of Fe and P found in soil, it has been shown that a spectral interference occurs with deuterium-arc background corrected GFAAS. The problem with the spectral interferences of Fe and P on Se have been eliminated by the use of Zeeman-effect GFAAS. Vapour generation AAS requires sample pre-treatment prior to analysis in order to achieve the correct oxidation state of Se whereas Zeeman-effect GFAAS can be used to analyse the digested sample solution directly with the use of a chemical modifier. Although the three different sample digestion procedures gave similar results, the $HNO_3 - H_2O_2 - HF$ and $HNO_3 - HCl - HF$ mixtures are preferred due to the potential hazards involved with $HClO_4$ and the tedious nature of the $HNO_3 - HClO_4 - HF$ procedure.

The good agreement between the values found by the Zeeman-effect graphite furnace and vapour generation AAS techniques for the determination of Se in soil and coal fly ash confirm the suitability of both the techniques for these analyses.

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