Some Studies with an Agilent VGA-76 Hydride Generator for Selenium Determination

Application Note

Atomic Absorption

Author

Dr. A.L. Gelman
Division of Agricultural Chemistry & Biochemistry
School of Agriculture
Aberdeen
Scotland

Introduction

From the mid 1960s the importance of selenium in animal nutrition became evident. By 1970, the necessity for selenium analysis of animal feedstuffs produced in the north of Scotland was obvious, and at that time the methodology available for selenium assay was either by fluorimetric methods or by an elaborate distillation followed by various colorimetric procedures. None of these methods lent themselves to the requirements for a routine method of selenium analysis. The methods were tedious, used a high degree of analytical skill, and often required a large sample because of the low sensitivity of the method.

With the introduction of hydride generation techniques for the determination of selenium, some of the above problems could be overcome, and though a fluorimeter was available, the determination of selenium at the School of Agriculture at Aberdeen University has been pursued by hydride generation coupled with atomic absorption spectroscopy for the last 12 years.

The work has been carried out using the various Agilent vapor generation kits. For about 10 years the Model 64 was used, modified to a certain degree, and while producing results, the matrix interference inherent in the zinc-gas generation necessitated the use of standard addition techniques for reliable results. This made the processing of routine analysis slow. In this unit selenium was estimated in a nitrogen-hydrogen entrained air flame. In 1982 the Model 65 was obtained and selenium assays were transferred to this equipment with improved accuracy, precision and speed of analysis. There seemed to be less matrix interference generating the hydride with sodium borohydride than with zinc.

Presently, work is being carried out using the Agilent VGA-76 hydride generator for selenium determination and the following are some observations on the use of this accessory for routine selenium analyses of a variety of agricultural feedstuff materials. Both the Model 65 and the VGA-76 vapor generators use an absorption cell located in the optical path of the atomic absorption spectrophotometer heated by a flame.

A critical aspect of any form of selenium assay is the sample preparation. Over the years from both personal experience and innumerable publications in the scientific press sample material must be wet ashed under carefully controlled temperature conditions, using a nitric acid, perchloric acid mixture, followed by treatment with 6 M hydrochloric acid to convert all the selenium present in the digest to Se (IV) oxidation state. Selenium hydride does not appear to be generated from Se (VI) oxidation state.

Outline of Sample Preparation

The sample 1 g is weighed into a digestion tube (Corning, 26 mm diam., 250 mm long, with constriction) containing a few anti-bumping granules (BDH) and to it is added 10 mL concentrated nitric acid. After standing overnight the tube is agitated on a Gallenkamp Spinmix and then placed in a temperature controlled block digestor (Technicon BD-20). The sample is digested for one hour at 130 °C and then at 150 °C for half an hour by which time the volume of solution is reduced to about 3 mL. The tube is removed from the block and 2 mL perchloric acid added. The digestion is then continued at 170 °C for a further one hour, by which time the volume is reduced to about 2 mL and the digest is clear. After cooling, 2 mL of distilled water is added to the digest and the tube heated for half an hour at 170 °C; this treatment is repeated once and in this way traces of nitric acid are removed from the digest. The digest is cooled and 4 mL of 40% v/v hydrochloric acid added to the tube which is then heated for half an hour at 90 °C converting the Se to the Se(IV) state. After cooling, the volume of digest is made to 10 mL with distilled water. This solution is now ready for assay.

Procedure for the Agilent 64 and 65 hydride units was similar except that the final volumes of acid and distilled water were doubled, for example the final sample volume was 20 mL.

If any charring of the sample occurs during this procedure, selenium is lost, and a repeat sample must be carefully processed. Apparently the selenium is reduced to elemental form and vaporised when charring occurs.

Instrumentation

Vapor generation accessory		Agilent VGA-76
Atomic absorption spectrophotometer		Agilent AA-875
Chart recorder		Agilent 9176
Sample changer		Agilent Model 51
Printer		Hewlett Packard HP82905A
Se hollow cathode lamp		Agilent
Integration times	automated analysis	8 seconds
	manual	4 seconds
Delay period	automated	35 seconds
	manual	40 seconds

Reagents

Nitric acid	Analar BDH
Perchloric acid	Analar BDH
Hydrochloric acid	Analar BDH
Sodium hydroxide	Analar BDH
Sodium borohydride pellets	Alfa-Ventron

The sodium borohydride pellets are dissolved in0.5% w/v sodium hydroxide solution to give a 0.6% w/v $NaBH_4$ solution.

Though this solution has a limited storage life at 5 °C, a volume (100–200 mL) of fresh solution is made up for each day's analysis.

Standard selenium stock solution. Dissolve 1.6330 of selenous acid (H2SeO3) in 200 mL distilled water, dilute to 1 liter to give 1000 mg Se liter-1. Store in a polythene bottle.

For routine assays the stock solution is diluted with distilled water. For standardisation of the system to tubes containing 2 mL perchloric acid, 4 mL 40% w/v hydrochloric acid 0.05, 0.10, 0.15, 0.20 µg of Se is added and the volume of each tube made to 10 mL with distilled water.

The stock solution has an excellent shelf life but serial dilution of the stock for standards is made daily.

To condition the system a solution prepared as above containing 0.50 µg Se is used.

Methods

The instrument and accessories are set up according to the operating instructions in the respective manuals. Unless otherwise stated, determinations are carried out in the Concentration mode.

Using the M-51 sampler which has a maximum sampling time of about 20 seconds, it was found that by removing the reaction coil in the VGA-76 system the sampler could be used, i.e. delay time was reduced, though there was a small loss in sensitivity. (Editor's note: "Modern programmable sample changers such as Agilent's PSC-55 enable analysts to select whatever sampling time is required.")

For selenium assays concentrated hydrochloric acid is used as the acid reagent.

The reaction coil was replaced by a jacketed glass coil and warm water passed through the jacket. There was a slight improvement in sensitivity and linearity of calibration when using this system. This modification was not persisted with, as the advantages were very limited.

Results

Four samples (A,B,C,D) of previously analysed herbage were examined. Final results are shown in Table 1 for individual digests. Part of the difference in each sample set could be due to variations in wet washing. The weight of sample taken for assay is shown. In the case of sample D, the sample solution after digestion was diluted with blank solution 1:5; Sample C, diluted 1:1.

Table 1. Results in µg/g Sample

Herbage sample	A (I.0 g)	B (I.0 g)	C (0.5 g)	D (0.5 g)
Replicate (1)	0.023	0.252	1.22	3.57
(2)	0.032	0.310	1.30	4.34
(3)	0.034	0.302	1.55	4.36
(4)	0.024	0.283	1.33	3.59
(5)	0.026	0.264	1.36	3.77
(6)	0.024	0.269	1.33	3.99
(7)	0.027	0.287	1.31	3.99
(8)	0.017	0.264	1.32	4.02
(9)	0.021	0.276	1.86	4.18
(10)	0.021	0.280	1.40	3.78
Mean	0.025	0.279	1.39	3.95
S.D.	0.00513	0.0178	0.175	0.281

Interference Experiment

The instrument was calibrated in the Concentration mode. Tubes containing the normal assay acid solutions and 0.1 µg Se were prepared. To these tubes various levels of copper, iron, manganese, chromium, zinc, and molybdenum were added. Table 2 shows the results of this experiment. A recovery of 0.1 µg Se would indicate no interference.

Table 2. Effect of Metals on Selenium Recovery

Selenium in tube (µg)	Element in tube (µg/mL)	Cu	Fe	Mn	Cr	Zn	Mo	Equivalent to element conc in 1 g sample (µg/mL)
0.1	0	.094	.103	.109	.105	.096	.096	0
0.1	1	.095						10
0.1	3	.097						30
0.1	6	.096						60
0.1	10	.088	.103	.106	.108	.093	.105	100
0.1	20		.103	.110	.110	.094	.105	200
0.1	40		.101	.106	.109	.094	.093	400
0.1	50	.028						500
0.1	100	.077	.096	.102	.093	.085	.068	1000

The effect of perchloric acid in the assay was not examined as earlier experiments showed that doubling the amount of the acid in the assay had no effect on calibration peaks.

The digestion process was omitted in this study.

The effect of nitric acid on the assay was examined. To tubes prepared as above, varying amounts of the acid were added:

HNO_3(%)	0	2	4	10	20
Se	.096	.094	.089	.089	.080

This is a strange result; the literature abounds with mention of the interference due to nitric acid, and in this case little effect is seen. No digestion was performed, and therefore perhaps no nitrate formation could occur to cause interference.

Comments

From the above results, it would seem that there is little interference of the assay by elements normally present in herbage. The marked interference by copper though must be noted, although most herbages have levels of copper well below the interfering levels. In the analysis of mineral mixtures high levels of various elements can be encountered and generate incorrect results.

Sensitivity and Detection Limit

This study was carried out in the Absorbance mode. Sensitivity found to be 0.0005 ppm Detection limit to be 0.00025 ppm

The measurement of a standard solution containing 0.1 µg of selenium 12 times gave a

Mean	0.099
S.D.	0.00213

Silage Analysis

A silage was analyzed, several individual digests made: Selenium found in ppm:

a	0.04	e	0.03	Mean	0.035
b	0.04	f	0.04	S.D.	0.0053
c	0.04	g	0.03		
d	0.03	h	0.03		

This sample of silage was analyzed by the method of standard additions, and the result found to be 0.032 ppm Se.

Standard Routine Analysis

An example of a standard routine analysis of several samples is presented in Table 3. The samples were all prepared for analysis according to the method outlined above, but weights of sample were taken according to sample type, for example, herbages 1 g, mineral mixes 0.5 g. If high values are encountered, samples are readily diluted with blank solution and their original concentration calculated.

The AA-875 was calibrated in the Concentration mode, and standards used were 0.1, 0.2, 0.3, 0.4 µg Se per tube.

Table 3. Results for Routine Analysis

Sample no.	Se	Sample no.	Se
1	0.026	21	0.038
2	0.021	22	0.025
3	0.021	23	0.026
4	0.022	24	0.025
5	0.024	25	0.026
6	0.026	26	0.023
7	0.024	27	0.023
8	0.027	28	0.023
9	0.283	29	0.065
10	0.267	30	0.063
11	0.269	31	0.059
12	0.287	32	0.055
13	0.332	33	0.068
14	0.341	34	0.084
15	0.333	36	0.066
16	0.327	356	0.072
17	0.359	37	0.184
18	0.377	38	0.085
19	0.394	39	0.076
20	0.399	40	0.066

Conclusions

From the work carried out so far, the VGA-76 unit has permitted an automated approach to the routine analysis of feedstuffs for selenium. The accuracy of the procedure is adequate for agricultural advisory purposes, and the precision of the method is high. The main source of inaccuracy appears to be sample digestion. In this procedure meticulous attention to the cleanliness of the digestion tubes is necessary. The tubes are rinsed after use, soaked in Decon, washed with tap water, and then soaked in 20% v/v nitric acid, followed by rinsing with distilled water. The treatment permits good duplication of results. A similar regime is necessary with the absorption cell and gas/liquid separator of the VGA-76 to maintain sensitivity.

In using the system, carry over from one sample to another can and does sometimes occur. This appears to be due to two factors (a) reaction continues in the gas/ liquid separator, and (b) the time taken for the liquid in the separator to be flushed out is excessive. This was seen by using a dye — it required about 5 or 6 “delay times” to clear it. (Editor’s note: “The later model gas/ liquid separator is designed to minimize flushing times”.) Before each analytical run, it is important to check flow rates of the pumping system and make sure these are adequate. In the paper by Welz & Melcher (Analyst 1983, 108, 213-224) a treatment for re-sensitising the absorption cell is described. This procedure was found to be very effective.

Over all, the system was found to be practical, easy to use, and adequate for the routine analysis of animal feedstuffs for selenium.

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