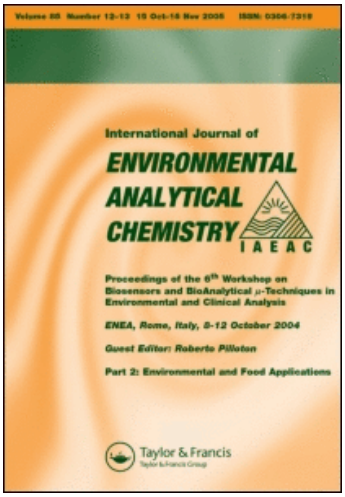

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Determination of Silver in Plants by Flameless Atomic Absorption Spectrometry and Neutron Activation Analysis

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Three analytical techniques suitable for determining silver concentrations in plants are presented and compared. Graphite furnace atomic absorption spectrometry performed directly on sample digests was the most sensitive and convenient. Neutron activation analysis, measuring ^{110m}Ag gave good reproducibility, but lower sensitivity. A cyclic activation scheme to generate and detect the short-lived isotope ^{110}Ag was useful as a quick reconnaissance technique, but interference from ^{76}As reduced its effectiveness.

Data are presented on the silver content of terrestrial plants. Background silver concentrations for lichens and bryophytes collected from Wales, U.K. were $<0.07\,\mu g\,g^{-1}$. Samples collected from areas contaminated by derelict metal mines contained between $0.1–1.0\,\mu g\,Ag\,g^{-1}$. The aerial portions of vascular species usually contained less silver than bryophytes growing on the same substrate. Fungi are shown to bioconcentrate silver to a greater extent than cadmium, copper or lead.

KEY WORDS: Silver, plants, graphite furnace atomic absorption spectrometry (GFAAS), Neutron activation analysis (NAA), Cyclic activation programme (CAS).

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INTRODUCTION

Silver is an element of increasing economic importance. Various prospecting techniques are being used as a means of biogeochemical exploration for ores.[1] These include analysis of plant material in which Ag concentrations are typically less than $1\,\mu g\,g^{-1}$ dry weight. Sensitive techniques are therefore required for routine analyses. This paper describes three methods for determining Ag at low concentrations. The first is a simple, reliable method using graphite furnace atomic absorption spectrometry (GFAAS). The other two methods employ neutron activation analysis (NAA), either by the conventional lengthy, single irradiation that generates ^{110m}Ag ($t_{1/2}$, 253 days), or by a cyclic activation programme (CAS), (which alternates the sample between the irradiation source and a detector), optimized for the short-lived isotope ^{110}Ag ($t_{1/2}$, 24 seconds).

Previously published data on Ag concentrations in plants relate to biogeochemical prospecting[2,3] and are consequently limited to information on relatively few species. Because the majority of studies have been conducted in mineralised areas little "baseline" data exist for Ag concentrations in plants, although Ag accumulation by certain species of fungi has recently received attention.[4–6]

The analytical techniques outlined above have been applied to a variety of plant species.[7] The Ag content of aquatic bryophytes from a mineralised area of west Wales, Great Britain, have been reported elsewhere.[8] In this paper we present and discuss methods for the analysis of Ag in plants, and selected data on Ag in terrestrial fungi, lichens, bryophytes and vascular plant species.

SAMPLE COLLECTION AND PREPARATION

Aerial parts of plants were collected in the field prior to sampling nearby or underlying soil. Vegetation was cut with carbon-steel scissors, placed in separate plastic bags and washed with double distilled water within 24 hours of collection. All samples were air dried at 80°C for a further 24 hours, ground in a small electric domestic-pattern grinder and stored in fresh paper envelopes at room temperature.

Samples for NAA were dry ashed in silica crucibles at 500°C for between 9 and 18 hours, i.e. until all organic matter had been oxidised. For GFAAS analysis, samples were either dry ashed prior to extraction with HNO_3 (Aristar Grade), or wet digested. Checks with standard additions (0.05–5 μg) of ^{110m}Ag on the wet digestion procedure gave recoveries >97%. Ashed vegetation samples for long irradiation were compressed into pellets by applying 7000 kg f in a stainless steel die. Pelletisation allowed a greater sample mass, typically 100–200 mg, to be placed in a capsule and easy transference of the sample to unirradiated capsules for counting. CAS samples were typically 100 mg.

Standards (0.1, 1.0, 10 μg Ag) were prepared on filter paper discs using $AgNO_3$ solutions. Plastic capsules, approximately 6 mm thick and 10 mm in diameter were used to contain all the samples and standards. Twelve capsules were placed into larger cylindrical polythene containers for irradiation.

The preparation of soils for analysis has been described elsewhere.[9]

ANALYTICAL TECHNIQUES

GFAAS

A Varian-Techtron model AA1475 spectrophotometer equipped with a GTA-95 graphite tube atomiser and autosampler, with oxygen free nitrogen as a purge gas and a silver hollow cathode lamp, was used for all analyses. An ashing temperature of 500°C preceded atomisation at between 2000–2500°C, depending on sample matrix.

Reagents Standard solutions of 10 ng Ag ml^{-1} were prepared from a stock solution of 1 mg Ag l^{-1} as $AgNO_3$ BDH Spectrosol grade. Normal calibrations or standard additions were prepared by the carousel autosampler from the 10 ng Ag ml^{-1} standard.

Performance data The sensitivity or Typical Characteristic Concentration (defined as the typical weight of the element which would produce a peak height of 0.004 absorbance) was measured at 0.9 pg for a 20 μl sample with a new pyrolytic coated graphite tube. The detection limit (measured as twice the standard deviation of the

solvent "blank") was 0.7 pg Ag. A linear calibration curve was obtained in 0.3M HNO_3 up to 0.250 absorbance units, corresponding to 0.05 ng Ag in a 20 μl sample with a zero gas flow at atomisation. The calibration did not curve markedly until above 0.5 absorbance units.

The Analytical Working Range (measured as 0.25–10 ng Ag ml^{-1}) was determined based on the Typical Characteristic Concentration. The lower value is the expected concentration which would give a response between 0.03 and 0.05 absorbance units for a 20 μl aliquot while the upper value is a response of 0.8 absorbance units, using a new pyrolytically coated tube.

Analytical Data Standard additions were routinely performed on each sample; spikes of 0.01, 0.02, 0.03 and 0.04 ng Ag were usually added from the autosampler stock solution. If matrix suppression of the Ag spike was strong then larger amounts of Ag were added.

Alteration of the sample volume injected (between 1–20 μl), the gas flow conditions at atomisation or dilution adjusted the sample absorbance value. An analyte absorbance between 0.03 and 0.1 was ideal, allowing standard additions to remain in the linear range of the calibration curve.

NAA

Irradiation and counting Samples and standards were irradiated at the Imperial College Reactor Centre under Cd in a flux of 1×10^{12} n cm^{-2} s^{-1} for 10 days over a period of a fortnight to generate ^{110m}Ag. The irradiated samples were then allowed to decay for between two and four weeks[10,11] to reduce background radiation (e.g. from ^{76}As at 657 keV, $t_{1/2}$, 1.1 days). The pelletised samples were then removed from the irradiated containers and capsules and transferred to unirradiated capsules for counting. The samples were analysed by γ-spectrometry using a Ge(Li) detector, coupled to a 4096 channel analyser, for a counting time of 6,000 or 10,000 seconds. Silver was detected at both 657 and 818 keV energies.

CAS

CAS repeatedly irradiates and counts samples to enhance the signal-

to-background ratio for the isotopes of interest.[12,13] Optimisation of the irradiation, decay and counting periods reduced the presence of interfering isotopes, while enhancing detection of the ^{110}Ag (657 keV). Each cycle (T) is a series of timed steps:

$$T = ti + tw + tc + tw' \quad (1)$$

where ti = time of irradiation
tw = delay
tc = time of counting
tw' = time between end of count and start of irradiation.

Two programmes were tested under a flux of 4.7×10^{10} n cm^{-2} s^{-1}.
$A = (ti\ 30\ s, tw\ 5\ s, tc\ 50\ s) \times 5$
$B = (ti\ 20\ s, tw\ 3\ s, tc\ 20\ s) \times 10$

Performance Data Table 1 summarises the performance data for the two activation analysis procedures. The sensitivity and detection limits of both techniques are similar, but do not approach those for GFAAS, whilst they remain as instrumental techniques, i.e. without radiochemical separation.

All three techniques were compared on samples of different species of fungi collected from Esher Common, a non-mineralised area of south east England. Some of these species of fungi are known to

TABLE I

Summary of performance data for activation analysis.

	Long irradiation ^{110m}Ag		Cyclic activation ^{110}Ag	
	657 keV	818 keV	*A* 657 keV	*B* 657 keV
Sensitivity (μg)[a]	0.03	0.30	0.01	0.015
Detection limit[b] (μg g^{-1} ash)	0.13	0.80	0.20	0.21

A CAS programme (*ti* 30s, *tw* 5s, *tc* 50s) × 5.
B CAS programme (*ti* 20s, *tw* 3s, *tc* 20s) × 10.
[a]Defined as the minimum mass of Ag which produces a peak area equal to twice the square root of the background area in an interference free matrix.
[b]Defined as the sensitivity divided by the product of sample mass and Ag peak area per unit Ag mass.

accumulate Ag[4,6] which enabled a comparison to be made across a wide range of concentrations. The results, presented in Table II, show good agreement between the techniques. GFAAS was the most sensitive, detecting 0.010 $\mu g\,Ag\,g^{-1}$ in Bowen's kale. In general, Ag concentrations were higher in accumulating species measured by CAS than by GFAAS (*Amanita fulva, A. muscaria, Russula sardonia, Boletus edulis* and *B. badius*), but this was reversed at low Ag levels (*Collybia maculata, Piptoporous betulinus, Armellaria mellea, Paxillus involutus*). There is some evidence to suggest that species which accumulate Ag may also accumulate As.[5] Thus, high concentrations of As (measured as ^{76}As) would cause an enhancement of the 657 keV γ-ray peak used for the analysis of ^{110}Ag (I. Valente, pers. comm.). However ^{110m}Ag, with 2–4 weeks delay before counting would not be affected by possible ^{76}As interference. Analyses by the

TABLE II

Ag content of fungi and Bowen's kale determined by three analytical techniques ($\mu g\,Ag\,g^{-1}$ dry weight).

	GFAAS	Cyclic activation[a]	Long activation	
			657 keV	818 keV
Amanita fulva	16.9	21.4	16.2	15.4
Collybia maculata	0.69	0.54	—	—
Amanita muscaria	5.62	7.6	5.37	4.83
Piptoporous betulinus	0.06	0.025	<0.026	<0.51
Armillaria mellea	1.31	0.98	0.98	0.87
Paxillus involutus	1.11	0.99	—	—
Leccinum aurantiacum	0.62	0.60	0.41	<0.44
Boletus badius	1.29	1.76	1.19	1.08
Russula sardonia	3.80	4.37	3.22	2.94
Boletus edulis	4.51	5.66[b]	4.59[c]	4.15[c]
Amanita rubescens	0.15	0.14	—	—
Bowen's kale	0.010[d]	ND	<0.043	<0.75

[a]Programme (*ti* 20s, *tw* 3s, *tc* 20s) × 10.
[b]Mean of six determinations: 5.66 ± 0.35 (RSD = 6%).
[c]Mean of five determinations:
at 657 keV, 4.59 ± 0.086 (RSD = 2%)
at 818 keV, 4.15 ± 0.39 (RSD = 9%).
[d]Mean published value is 0.019 $\mu g\,Ag\,g^{-1}$.
— not determined due to insufficient sample.
ND = not detectable.

long irradiation procedure were consistently lower than by either GFAAS or CAS. Of the two energies, 818 keV was the least sensitive (see Table I) and detected consistently lower concentrations of Ag. NAA using the long irradiation procedure at 657 keV gave the most reproducible results (2% RSD on 4.6 $\mu g\,Ag\,g^{-1}$, counting error on 1 $\mu g\,Ag\,g^{-1}$, ca 1.4%) but all methods had an RSD < 10% at these concentrations.

SUMMARY OF DATA

This section reviews information on the Ag content of terrestrial plant species.

Fungi

Soil underlying the fungi listed in Table II had an Ag content of 0.04 $\mu g\,g^{-1}$ in the A horizon. The fresh litter, humus and active rhizosphere contained 0.045, 0.095 and 0.28 $\mu g\,Ag\,g^{-1}$ respectively. For species recorded in Table II and other species recorded elsewhere[7] enrichment factors (Sporophore/A horizon) were between 1.5–420 (mean 62) for Ag (see Table III). This ability to bio-concentrate Ag was considerably greater than that shown for Cd (enrichment factor 2.3–179, mean 25), Cu (1–15, mean 5.6) or Pb (0.14–1.8, mean 0.70) and suggests fungi may be significant in enriching Ag in the surface soil horizons.[14]

TABLE III

Mean and range of silver contents of plant phyla and plant: soil ratios recorded during this study.

	Ag ($\mu g\,g^{-1}$ d.w.)		Plant: soil ratio	
	Mean	Range	Mean	Range
Fungi	10	0.064–121	4.9	0.1–24
Lichens	0.6	0.039–3.64	0.15	0.008–0.4
Bryophytes	1.0	0.028–7.0	0.39	0.013–1.6
Pteridophytes	0.024	0.008–0.041	—	0.008–0.046
Vascular plants	0.015	0.008–0.99	0.011	0.002–0.15
Mixed grassland communities	0.01	0.011–0.29	0.017	0.008–0.038

Fungi growing in contaminated soil ($5.0\,\mu g\,Ag\,g^{-1}$) near a derelict Pb-Ag mine in Wales contained higher Ag concentrations than any other phylla recorded during this study. The highest concentrations were found in two species of the Agaricales, (*Hygrocybe coccineus*, $121\,\mu g\,Ag\,g^{-1}$; *Agaricus macrosporus*, $30\,\mu g\,Ag\,g^{-1}$) and a member of the Boletales (*Gomphidius roseus*, $23\,\mu g\,Ag\,g^{-1}$). Other workers [4–6] have also found the highest Ag concentrations in members of these families (and the Lycoperdales). The ability to accumulate Ag can vary considerably with a genus, as is illustrated by the *Amanita* data (see Table II).

Lichens and Bryophytes

Lichens and mosses from uncontaminated sites in Wales contained $<0.07\,\mu g\,Ag\,g^{-1}$. The lowest concentrations recorded were for a specimen of the lichen *Cladonia gracilis* ($0.039\,\mu g\,Ag\,g^{-1}$) and the moss *Rhytidiadelphus triquestris* ($0.029\,\mu g\,Ag\,g^{-1}$). These values are very similar to those from other "baseline" sites in Europe.[10,11] Terrestrial and epiphytic species from the southern hemisphere may contain lower concentrations.[15]

Most species of lichens and mosses collected in close proximity to Welsh Ag mines had concentrations in the range $0.1–1.0\,\mu g\,Ag\,g^{-1}$, which is in close agreement with data from sites in Norway[11] and New Zealand[15] subject to sources of aerial contamination. The highest concentrations recorded in this study were $0.14–3.6\,\mu g\,Ag\,g^{-1}$ in specimens of *Peltigera canina* and $0.7–7.0\,\mu g\,Ag\,g^{-1}$ in *Polytrichum commune* collected near sites subject to aerial deflation of mine spoil.

Vascular plants

Silver concentrations in the aerial portions of vascular plants (herbaceous and shrub species) were, on average, lower than those in fungi, lichens and mosses (see Table III). Concentrations varied considerably within particular species. For example, *Calluna vulgaris*, a species ubiquitous in the Welsh uplands, contained between $0.037–0.39\,\mu g\,Ag\,g^{-1}$ when grown on contaminated soils of $1.4–9.2\,\mu g\,Ag\,g^{-1}$. Limited data for individual species (e.g. *Brassica napus*, *Ulex europaeus*, *Calluna vulgaris*) growing on soils with a range of Ag concentration showed no correlation between total soil and plant Ag content.

CONCLUSIONS

The three techniques reported here provide a useful analytical cross-check; thirty samples a day may be analysed using GFAAS which is the preferred technique because of its sensitivity and convenience. CAS is a useful rapid reconnaissance method, capable of processing sixty samples a day. NAA detecting ^{110m}Ag may be the most reproducible of the three methods and has a multi-element analytical capability.

Fungi were the only phylla able to bioconcentrate Ag, and this was particularly evident in members of the Boletales and Agaricales. The bioconcentration of Ag was considerably greater than for other metals analysed, namely Cd, Cu and Pb. A specimen of *Amanita fulva* (Agaricales) growing on uncontaminated soil contained $17\,\mu g\,Ag\,g^{-1}$, while specimens of *Hygrocybe coccineus*, *Agaricus macrosporus* (Agaricales) and *Gomphideus roseus* (Boletales) growing on contaminated soils contained 120, 30 and $23\,\mu g\ Ag\,g^{-1}$, respectively.

Bryophytes and lichens growing in uncontaminated locations in Wales contained $<0.07\,\mu g\,Ag\,g^{-1}$. Available data confirm Shacklette's[16] observation that bryophytes contain higher concentrations of Ag than vascular plants growing on the same substrates (see Table III).

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