

2.6 SOILS, PLANTS AND FERTILIZERS

2.6.1 Introduction

Two recent reviews provide valuable surveys of the use of all analytical techniques in these areas. Dinnin (*Anal. Chem.*, 1975, **47**, (5), 97R) discussed the analysis of inorganic and geological materials covering methods of sample preparation as well as techniques for measurement. This extensively-referenced article can be recommended to anyone seeking an overall view of the field for the manner in which it puts into perspective the battery of analytical techniques now available for tackling a given problem. Similarly, Gehrke and Rexroad (*Anal. Chem.*, 1975, **47**, (5), 42R) have reviewed work on fertilizer analysis in 1973 and 1974, paying particular attention to the determination of N, P and K but also dealing with minor and trace nutrients. For on-line quality control purposes, automated molecular absorption methods are normally preferred for the major components while atomic spectroscopy finds most use in the determination of other elements, e.g. Ca, Co, Cu, Fe, Mg, Mn, Mo and Zn. Fertilizer analysis has also been reviewed elsewhere (516), as has the determination of many elements in soil and plant material (517, 518, 519, 520, 521).

In general, analytical interest appears to be concentrated on extraction methods with AAS normally regarded as a standard method for the final determination. In many instances, of course, analysis serves simply as a means of obtaining information of agronomic, horticultural or environmental interest (see, for example, 1407, 1409, 1411, 1415–1426, 1428–1431, 1433–1439, 1442–1446). The only use of AFS noted (273) had as its main purpose to demonstrate the applicability of the technique to a real sample, viz. orchard leaves.

If the beginning of a trend can be discerned in these areas it may be towards the adoption of plasma emission spectroscopy as a means of completing analyses (1454). This technique has the obvious advantage over AAS of simultaneous multi-element capability with wide dynamic ranges but, in view of the convenience and widespread acceptance of AAS and arc/spark AES, one cannot envisage an overnight change in the practice of most analysts. Commercial equipment is now available but the capital outlay required is likely to restrict its purchase to users with a high sample throughput, involving determination of several elements in each sample, who can use its capabilities fully. As development work on plasmas continues, however, one can foresee the technique becoming relatively more attractive and chemists are well advised to keep in touch with progress in this field.

2.6.2 Sample Preparation

Numerous methods are in everyday use for preparation of samples for determination of total or "available" content of metals in materials of agricultural interest. Since the variety of questions to be answered is large, there is no likelihood of universal standardisation of methods although valuable work on inter-comparison of techniques is reported each year. This provides an individual with a store of information and experience on which to base his choice of method for solution of his particular problems.

Wimberley (569) and Carel (934) have each studied the determination of total Hg in soils, releasing the metal by heating either an induction furnace or a thermogravimetric balance assembly and collecting the Hg vapour by amalgamation on gold. A fusion technique employing borax and NaOH has been recommended (537) for preparation of soil samples for AAS determination of total Ca, Mg and Mn. Extraction with CaCl_2 solution has been used in the determination of plant-available Mg (533) and Al and Mn (359) while other workers (266) have preferred an H_2SO_4 extraction for Mn. For trace elements, e.g. Co, Cu, Ni, Pb and Zn, extraction with APDC into MIBK has been used prior to AAS determination (114, 354). Sinha and Banerjee (1525), however, have found that a digestion

procedure involving evaporation with HF at 200°C, eliminated the need for lengthy extraction procedures in this type of determination. A noteworthy paper (1428) describes the extraction of stable organic complexes of Al, Ca, Cu, Fe and Mg from volcanic soils. Finally, Woodrill *et al* (1147) have reported a simple method in which the soil water is separated from the soil itself by centrifugation with CCl_4 . The upper, water layer is then available for determination of micro-nutrients by AAS in an electro-thermal atomizer.

For analysis of organic materials, such as plants, wet- or dry-ashing techniques can be used (391) and Isaac and Johnson (1181) have compared their efficiency concluding that both can be satisfactory for determination of Ca, Cu, Fe, K, Mg, Mn and Zn. Other workers, however, have found (783) that dry-ashing at 450–500°C caused volatilization losses in determination of Cd in tobacco and low results in comparison with those obtained after wet- or low-temperature plasma-ashing. Ganje and Page (2) also preferred wet-ashing with $\text{HNO}_3/\text{HClO}_4$ and used an electrothermal atomizer to obtain a lower limit of detection ($0.01 \mu\text{g g}^{-1}$) for determination of Cd in plant tissue but others have found (983) dry-ashing at 450°C to be satisfactory. Further examples of the successful use of wet-ashing in this area have included determination of As, Cr, Cu and Zn in preserved wood (281), Pb in roadside plants (56), Cr in Plants after extraction as the 2,4-pentanedione complex into CHCl_3 (1180) while Faithfull (1059) has described an automated system for detection of Fe in herbage *via* Kjeldahl digestion. Koirtjohann *et al* (*Anal. Chem.*, 1975, **47**, 1475) described the wet ashing of various organic samples in a microwave oven. Morris (142) has shown that Si can be solubilized rapidly from tobacco leaf by treatment with HIF or a fluoboric-boric acid system, while several reports (227, 878, 879, 1217) have appeared describing hydride generation as a preliminary to the AAS determination of As and/or Se. Finally, a combined liquid chromatography–AAS method has been used (889) for fractionation and determination of free and chelated Zn in plant tissue extracts.

Relatively few papers on analysis of fertilizers have been noted. Methods for determination of B by measurement of the BO_2 band emission in an air/ H_2 flame after extraction by the common 2,ethyl-1,3-hexanediol procedure (1183) and Hg by cold vapour AAS (320) have been presented. An interesting method (870) for determination of $\text{Ca}(\text{NO}_3)_2$ in $\text{CaNH}_4(\text{NO}_3)_3$ which depends upon the solubility of the former in methanol has also been described.

2.6.3 Atomic Absorption Spectroscopy

As noted above, most work has been concentrated on methods of sample preparation rather than on analytical measurement techniques. Most analyses are still performed by “conventional” AAS (1258), and Faithfull’s automation of this technique (1059) has already been noted. Several applications of electrothermal atomizers (2, 236, 1147, 1218, 1341) demonstrate that this approach may have advantages in some circumstances, *e.g.* if sample size is limited, concentration level is low, *etc.* Development of the “matrix modification” technique (232, 706 and Part I, Section 2.6) in which large excess of a selected compound is added to obtain the metal of interest in a convenient matrix before atomization, is likely to increase the acceptance of electrothermal atomization as an everyday technique.

2.6.4 Atomic Emission Spectroscopy

The comment was made in 2.6.1 that interest is beginning in the evaluation of plasma emission spectroscopy as a method for routine analysis of many elements in large numbers of samples, Scott *et al* (181, 304) have used an inductively-coupled plasma (1kW power) for determination of several elements, *e.g.* Al, B, Co, Cu, Fe, Mn, Ni, Pb, Zn in soils and/or

plant materials and showed that for some of these elements, this method was more accurate than flame AAS. The applicability to B is a particular advantage of this technique over flame methods for which an inconvenient extraction procedure is normally needed and this has been exploited (1453) for determining water-soluble B in fertilizers. Jones (1182) has reported a valuable collaborative study of the elemental analysis of plant material by the rotating-disc spark technique which shows RSDs between 0.059 (for Mg) and 0.89 (for Na). Despite this poor precision—18 out of 70 RSDs were above 0.3— the method has been accepted as “Official First Action” by the AOAC. Other interesting applications of emission spectroscopy in this area have included the use of a rotating briquetted disc for determination of elements including B in plant material (1466), use of a glow discharge lamp for determining macrocomponents (Si, Fe, Al, P, Mg and Ca) in soil (1512) and a comparison of different analytical techniques for analysis of various elements in soil extracts (1490). The automated flame AES determination of K in fertilizers has been described (1184) but, although this technique may be very satisfactory in a laboratory, one could have reservations, on safety grounds, over its use in preference to a molecular absorption technique in a fertilizer manufacturing plant.

TABLE 2.6 SOILS, PLANTS, FERTILIZERS

Element	λ/nm	Matrix	Concentration	Tech.	Analyte form	Sample treatment	Atomization	Ref.
Ag	328.1	Soils	Trace levels	A	L	Digest with 4 M HNO_3 + 1 M HCl. For Cu and Zn, buffer to pH 4.8 with acetate and extract with APDC/MIBK	F Air/ C_2H_2	354
Al	—	Tree foliage	—	A	L	(a) Ash and extract with HCl (b) Extract directly with H_4EDTA . (Comparison of treatments. La (0.1%) added as releasing agent. Method (a) preferred.)	F $\text{N}_2\text{O}/\text{C}_2\text{H}_2$	190
Al	308.2	Plants	80-240 $\mu\text{g/g}$	E	L	Dry, ash at 500°C, extract with HNO_3 (50%), evaporate to dryness, re-ash at 500°C and dissolve in HNO_3	P Induction-coupled plasma (27 MHz, 4 KW)	304
Al	—	Soils, plants	—	A	L	Extract soils by shaking for 5 minutes with 0.01 M CaCl_2 (1:2). Allow to settle and spray supernatant liquid. Extract plant ashes with HCl. (Methods for plant-available Al and Mn).	F —	359
Al	—	Soils, plants	—	—	—	Bibliography, 36 refs	—	521
Al	—	Soils	—	E	L	Equilibrate with $\text{H}_2\text{O}/\text{HCl}/\text{Ca}(\text{OH})_2$, filter and acidify with HCl	F $\text{N}_2\text{O}/\text{C}_2\text{H}_2$	1430
As	193.7	Tobacco	From 50 ng/g	A	L	Digest with $\text{HNO}_3/\text{HClO}_4$. Convert As(V) to arsine and freeze out in liquid- N_2 u-trap. Re-heat and pass to flame	F —	227
As	—	Preserved wood	—	A	L	Extract with $\text{H}_2\text{SO}_4/\text{HNO}_3$ and digest with H_2O_2	F —	281
As	—	Herbage	Trace levels (As III and As V)	A	G	Generate arsine by Na BH_4 reduction (a) from 1 M HCl (total As) and (b) from solution at pH 3-5 (As III)	F —	878
As	—	Soils, waters, aquatic organisms	—	A	G	Digest with $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$ (20:1:4), add NaBH_4 to 20% HCl solution and collect AsH_3H_2 in balloon, before transfer to flame with Ar	F Ar/ H_2	1409
B	249.8	Plants	25 $\mu\text{g/g}$	E	L	See Al, ref. 304	P —	304
B	—	Soils, plants	—	—	—	Bibliography, 24 refs	—	520

B	518 (band)	Fertilizers	0.1-10%	E	L	Complex acid-soluble B with 2-ethyl-1,3-hexanediol and extract into MIBK	F	Air/H ₂	1183
B	249.8	Fertilizers	From 0.001%	E	S	Extract with H ₂ O	P	ICP	1453
B	540 (band)	Plants	23 µg/g	A	L	Digest with HNO ₃ /HCO ₄ (1:1). Treat aliquot with H ₂ SO ₄ /acetic acid + curcumin/acetone. Add C ₂ H ₅ OH, centrifuge to remove Ca and measure at 540 nm, using Na hollow-cathode as radiation source	—	—	1522
Ca	422.7	Tree foliage	—	A	L	See AI, ref. 190	F	Air/C ₂ H ₂	190
Ca	—	Plant ash	—	E	L	Extract with HCl and add LaCl ₃	F	—	323
Ca	—	Soils, plants	—	—	—	Bibliography, 36 refs.	—	—	518
Ca	—	Soils	1%	A	L	Add La buffer	F	N ₂ O/C ₂ H ₂	537
Ca	—	Ca/NH ₄ NO ₃ fertilizers	—	A	L	Stir with CH ₃ OH, filter, wash and dilute with H ₂ O	F	—	870
Ca	—	Plant roots	—	A	L	Ash at 570°C for 2 hours, dissolve in HCl, dilute and add Sr (for Ca, Mg)	F	—	1422
Ca	—	Soils	—	A	L	Extract with CaCl ₂ /KCl and centrifuge	F	—	1427
Ca	—	Soils, earthworms	0.005-2.2%	A	L	Shake dried material with H ₂ O, stand, centrifuge, concentrate liquor by evaporation, treat residue with 2.5% acetic acid, centrifuge and digest residue with HNO ₃ . Evaporate extracts to dryness and dissolve in 0.1 N HNO ₃ + 6500 µg/ml LaCl ₃ (for Ca)	F	—	1439
Cd	228.8	Plant tissue	0.01-50 µg/g	A	L	Dry for 48 hours at 70°C, grind and treat (100 mg) with HNO ₃ /HClO ₄ . Dilute to volume (50 ml) and take 25 µl sample	Graphite furnace (HGA-2000)		2
Cd	—	Orchard leaves, environmental samples	—	F	L	Study of scatter-correction system	F	Air/C ₂ H ₂ or Ar/H ₂	773
Cd	—	Tobacco	—	A	L	(a) Dry-ash at <500°C (b) digest with HNO ₃ /H ₂ SO ₄ /H ₂ O ₂ (c) Low-temp. plasma ash. Comparison of treatments. Use (c), with extraction of Cd by dithizone/MIBK	F	—	783

TABLE 2.6 SOILS, PLANTS, FERTILIZERS — continued

Element	λ /nm	Matrix	Concentration	Tech.	Analyte form	Sample treatment	Atomization	Ref.
Cd	228.8	Wheat	0–150 ng/g	A	L	Ash at 450°C and dissolve in 1 M HNO ₃	Graphite furnace (HGA-70)	983
Cd	—	Soils	—	A	L	Extract with H ₂ O and concentrate Cd, Zn by dithizone/CCl ₄ extraction (pH 4–10)	F —	1446
Co	240.7	Soils	—	A	L	Buffer soil extract with citrate (pH 7.8–8.3) to mask Fe, and extract Co, Ni, Pb with APDC/MIBK	F —	114
Co	345.3	Soils	4–40 µg/g	E	L	Digest with HNO ₃ /HCO ₃ at 180°C for 1 hour. Cool, dilute to volume and decant supernatant liquid, for ultrasonic nebulisation. Results compared with those of flame AAS	P Induction-coupled argon plasma (1 KW)	181
Co	—	Plants	From 10ng/g	A	L	—	Graphite furnace	1243
Co	240.7	Soils	Trace levels	A	L	Evaporate with HF at 200°C	F —	1525
Cr	—	Preserved wood	—	A	L	See As, ref. 281	F —	281
Cr	357.9	Soils and sediments	0–4 µg/g	A	L	Extract with HCl. Add K ₂ SO ₄ to samples and standards to remove interference by Fe, Ti, V, Ni, Co and add Al to remove interference by Mg, Ba	F Air/C ₂ H ₂	307
Cr	357.9	Plants	From 5 ng/g	A	L	Wet-ash with HNO ₃ /H ₂ SO ₄ /HClO ₄ , extract Cr with 2,4-pentanedione into CHCl ₃ . Evaporate and redissolve in MIBK	F Air/C ₂ H ₂	1180
Cu	324.7	Soils	5–2000 µg/g	E	L	See Co, ref. 181	P —	181
Cu	324.7 Plants 327.4	Plants	2.2–6.4 µg/g	A	L	Digest ground sample with HNO ₃ /HClO ₄ . Heat in stages to 200°C, dissolve residue in 3% HClO ₄ and extract Cu with APDC/MIBK. Method for small samples (<0.05 g)	Graphite furnace (HGA-72)	236
Cu	—	Preserved wood	—	A	L	See As, ref. 281	F —	281
Cu	324.7	Plants	4–18 µg/g	E	L	See Al, ref. 304	P —	304
Cu	324.7	Soils	Trace levels	A	L	See Ag, ref. 354	F Air/C ₂ H ₂	354
Cu	—	Soils, plants	—	—	—	Bibliography; 64 refs.	—	519

Cu	—	Plant leaves	10-500 µg/g	A	L	Dry, homogenize, ash and redissolve. (Development of series of analysed plant standards)	F	—	1267
Cu	—	Soils, plants, manures, waters	—	A	L	Extracts soils with DTPA. Digest plants, evaporated waters and manures with $\text{HNO}_3/\text{HClO}_4$	F	—	1435
Cu	—	Barley soils	—	A	L	Digest plants with $\text{HNO}_3/\text{HClO}_4$ (2:1). Extract soils (various methods)	F	—	1436
Cu	—	Plants, tissues	—	A	L	Digest with $\text{HNO}_3/\text{HCO}_4$ (4:1), evaporate to dryness and dissolve in 3% HCl	F	—	1445
Cu	324.7	Soils	Trace levels	A	L	See Co. ref. 1525	F	—	1525
Fe	372.0	Plants	90-180 µg/g	E	L	See Al, ref. 304	P	—	304
Fe	—	Soils, plants	—	—	—	Bibliography; 72 refs.	—	—	517
Fe	248.3	Herbage extracts	70-200 µg/l	A	L	Dilute Kjeldahl extract with H_2SO_4 (30% w/v)	F	$\text{Air/C}_2\text{H}_2$	1059
Fe	—	Plant leaves	10-500 µg/g	A	L	See Cu, ref. 1267	F	—	1267
Fe	—	Plants	—	A	L	Digest with $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$	F	—	1416
Fe	—	Plants	—	A	L	Digest with $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$	F	—	1420
Fe	—	Soils	—	A	L	Shake with 0.0125 M CaCl_2 , add metal chelate (EDTA or EDDHA), centrifuge or leach soil in column with 0.025 N $\text{Ca}(\text{NO}_3)_2$ at pH 7.1-7.2. Add 0.05 N $\text{Ca}(\text{NO}_3)_2$ + metal chelate and collect effluent	F	—	1431
Fe	—	Soils	—	A	L	Extract with acid NH_4 oxalate, neutral Na dithionate and HCl (1:1)	F	—	1434
Fe	—	Soils, plants, manures, waters	—	A	L	See Cu, ref. 1435	F	—	1435
Fe	—	Barley soils	—	A	L	See Cu, ref. 1435	F	—	1436
Fe	—	Soils, plants	—	A	L	Extract soil solution in "Baroid" press and acidity with HCl. Digest plants with $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HClO}_4$ (10:1:4), filter and dilute. Prepare plant extracts from treatment with buffer solution (pH 6.1) of 0.2 N $\text{K}_2\text{HPO}_4/0.2$ N KH_2PO_4 . Grind, centrifuge, filter and acidity with HCl	F	—	1437

TABLE 2.6 SOILS, PLANTS, FERTILIZERS — continued

Element	λ /nm	Matrix	Concentration	Tech.	Analyte form	Sample treatment	Atomization	Ref.
Fe	—	Plants, tissues	—	A	L	See Ca, ref. 1445	F —	1445
Hg	253.7	Fertilizers	Up to 2.5 $\mu\text{g/g}$	A	G	—	Cold vapour	320
Hg	253.7	Soils, ores, organic materials	ng/g levels	A	S/G	Heat to 1000°C in induction furnace, pass vapour through $\text{K}_2\text{CO}_3/\text{Mg}(\text{ClO}_4)_2$ trap and collect Hg on Au-plated wire. Heat to release Hg for absorption measurement	Cold vapour	569
Hg	253.7	Soils	0–50 ng/g	A	G	Pass N_2 -stream over heated soil, and collect Hg on Au screen, after passage through $\text{K}_2\text{CO}_3/\text{Mg}(\text{ClO}_4)_2$ scrubber. Heat screen to volatilize Hg	Cold vapour	954
K	—	Plant ash	—	E	L	See Ca, ref. 323	F —	323
K	766.8	Fertilizers	0–60 $\mu\text{g/g}$ (in extract)	E	L	Add La to suppress P interference and add Li as internal standard	F —	1164
K	—	Plant roots	—	E	L	See Ca, ref. 1422	F —	1422
K	—	Soils	—	E	L	See Ca, ref. 1427	F —	1427
K	—	Micaceous colloids	—	E	L	Digest with HF/HClO_4 (Study of As retention by hydroxy-Al)	F —	1432
K	—	Plants, soils	—	E	L	Digest plants with H_2SO_4 , dilute and add Li internal standard. Extract soils with 1 N NH_4 acetate (pH 7)	F —	1433
Mg	—	Plant ash	—	E	L	See Ca, ref. 323	F —	323
Mg	—	Soils, plants	—	—	—	Bibliography; 36 refs.	—	518
Mg	—	Soils	—	A	L	Extract with 0.025 N CaCl_2	F	533
Mg	—	—	1%	A	L	See Ca, ref. 537	F	537
Mg	—	Plant roots	—	A	L	See Ca, ref. 1422	F —	1422
Mg	—	Plants	—	A	L	Ash at 500–550°C and dissolve in HCl	F —	1423
Mg	—	Soils	—	A	L	See Ca, ref. 1427	F —	1427
Mn	—	Soils	—	A	L	Extract with 0.1 N H_2SO_4 for 3 minutes	F —	266
Mn	403.3	Plants	40–100 $\mu\text{g/g}$	E	L	See Al, ref. 304	P —	304
Mn	—	Soils, plants	—	A	L	See Al, ref. 359	F —	359
Mn	—	Soils, plants	—	—	—	Bibliography; 72 refs.	—	517

Mn	—	Soils	0.05-0.1%	A	L	See Ca, ref. 537	F	N ₂ O/C ₂ H ₂	553
Mn	—	Plant leaves	10-500 µg/g	A	L	See Cu, ref. 1267	F	—	1267
Mn	—	Plants, soils	—	A	L	Ash at 450°C, extract with 6 N HCl (plants) or extract with 1 N NH ₄ acetate (soils)	F	—	1418
Mn	—	Plants	—	A	L	See Fe, ref. 1420	F	—	1420
Mn	—	Plants	—	A	L	See Mg, ref. 1423	F	—	1423
Mn	—	Soils, plants, manures, waters	—	A	L	See Cu, ref. 1435	F	—	1435
Mn	—	Barley soils	—	A	L	See Cu, ref. 1436	F	—	1436
Mn	—	Soils, plants	—	A	L	See Fe, ref. 1437	F	—	1437
Mn	—	Oats, fertilizers	—	A	L	Dry-ash plants at 470°C and dissolve in HCl. Extract fertilizers with H ₂ O	F	—	1438
Na	—	Fertilizers	—	E	L	—	F	—	277
Na	—	Plant roots	—	E	L	See Ca, ref. 1422	F	—	1422
Na	—	Soils	—	E	L	See K, ref. 1433	F	—	1433
Ni	232.0 Soils	—	—	A	L	See Co, ref. 114	F	—	114
Ni	351.5 Soils	—	1-1000 µg/g	E	L	See Co, ref. 181	P	—	181
Ni	—	Plants	0-50 µg/g	A	L	Add H ₂ SO ₄ , ash at 450°C for 24 hours, dissolve in HNO ₃ , evaporate, re-ash at 500°C and dissolve in HNO ₃	F	—	1411
Pb	—	Soils, plants	—	A	L	Extract soil samples with 0.2% acetic acid to determine available Pb. For total Pb, digest with HNO ₃ . Wet-ash plant samples with HNO ₃ /HClO ₄	F	—	56
Pb	217.0 Soils	—	—	A	L	See Co, ref. 114	F	—	114
Pb	405.8 Soils	—	—	E	L	See Co, ref. 181	P	—	181
Pb	283.3 Soils	Trace levels	—	A	L	See Ag, ref. 354	F	Air/C ₂ H ₂	354
Pb	—	Plant and soil extracts	—	A	L	Extract with HCl/NH ₄ F. (Study of extractable Pb in relation to soybean)	F	—	1365
Pb	—	Plants	—	A	L	Heat slowly to 490°C, ash for 4 hours, extract with 3 N HCl and dilute	F	—	1366
Pb	—	Soil, earthworms	3 µg/g-1.2%	A	L	See Ca, ref. 1439	F	—	1439

TABLE 2.6 SOILS, PLANTS, FERTILIZERS — continued

Element	λ/nm	Matrix	Concentration	Tech.	Analyte form	Sample treatment	Atomization	Ref.
Pb	217.0	Soils	10 $\mu\text{g/g}$ –1.5% (dry weight)	A	L	Extract with 0.6% (w/v) HCl or conc. HNO_3 . Evaporate to reduce bulk	F —	1442
Pb	—	Soils, plants	0.5–500 $\mu\text{g/g}$	A	L	Digest soils with HF/HNO_3 (1:1). Dry-ash plants at 450°C and dissolve in 2 M HCl	F —	1443
S (SO_4)	870	Superphosphate fertilizers (Ba)	—	E	L	Add excess BaCl_2 and determine residual Ba ion.	F —	419
Se	196.0	Plants	10–400 ng/g	A	L, G	Digest with $\text{HNO}_3/\text{HClO}_4$, dilute with 50% HCl and add NaBH_4 . Sweep Se hydride to flame in stream of N_2	F H_2/Air or H_2/N_2	879
Si	—	Tobacco leaf	—	A	L	Treat cured leaf with 48% HF. Add H_3BO_3 to form interference-free matrix	F $\text{N}_2\text{O}/\text{C}_2\text{H}_2$	142
Si	—	Tree foliage	—	A	L	See Al, ref. 190	F $\text{N}_2\text{O}/\text{C}_2\text{H}_2$	190
Zn	213.8	Soils	1–1000 $\mu\text{g/g}$	E	L	See Cu, ref. 181	P —	181
Zn	—	Preserved wood	—	A	L	See As, ref. 281	F —	281
Zn	213.9	Plants	13–23 $\mu\text{g/g}$	E	L	See Al, ref. 304. For Zn, match standards for Ca, K, Mg content	P —	304
Zn	213.8	Soils	Trace levels	A	L	See Ag, ref. 354	F $\text{Air}/\text{C}_2\text{H}_2$	354
Zn	—	Soils, plants	—	—	—	Bibliography; 64 refs.	—	519
Zn	—	Orchard leaves, environmental samples	—	F	L	See Cd, ref. 773	F $\text{Air}/\text{C}_2\text{H}_2$ or Ar/H_2	773
Zn	—	Plant tissues	—	A	L	Separate metal ion or chelate by liquid chromatography and pass eluate directly to nebulizer for continuous monitoring ('LCAAS' method)	F —	889
Zn	213.9	Wheat	0–50 $\mu\text{g/g}$	A	L	See Cd, ref. 983	F $\text{Air}/\text{C}_2\text{H}_2$	983
Zn	—	Plant leaves	10–500 $\mu\text{g/g}$	A	L	See Cu, ref. 1267	F —	1267
Zn	—	Plants	—	A	L	See Fe, ref. 1420	F —	1420
Zn	—	Soils	—	A	L	See Fe, ref. 1431	F —	1431
Zn	—	Soils, plants, manures, waters	—	A	L	See Cu, ref. 1435	F —	1435
Zn	—	Barley soils	—	A	L	See Cu, ref. 1436	F —	1436

Zn	—	Soils, plants	—	A	L	See Fe, ref. 1437	F	—	1437
Zn	—	Soil, earthworms	0.2 µg/g–0.13%	A	L	See Ca, ref. 1439	F	—	1439
Zn	—	Plants, tissues	—	A	L	See Cu, ref. 1445	F	—	1445
Zn	—	Soils	—	A	L	See Cd, ref. 1446	F	—	1446
Zn	213.9	Soils	Trace levels	A	L	See Co, ref. 1525	F	—	1525
Various (6)	—	Agricultural products	Trace levels	A	L	Review of methods for "total" and "available" toxic elements (Cd, Cu, Pb, Hg, Ni, Zn) in plant products	F	—	391
Various	—	Soils, rocks	—	E	S	—	A	Gas-sheathed D.C. arc	174
Various	—	Fertilizers	—	—	—	Bibliography, 1966–1974	—	—	516
Various (11)	—	Orchard leaves	—	A	L	Digest with HNO ₃ /HClO ₄	F	Air/C ₂ H ₂	553
Various (10)	—	Soils, plants	ng/g levels (Pb, Cd)	A	L	Prepare soil extracts or plant digests and analyse directly for all elements except Pb, Cd. For these, extract with APDC or dithizone, respectively, evaporate with HNO ₃ and redissolve in HCl	F	—	877
Various (7)	—	Soils	—	A	L	Complex and concentrate by biuret extraction. (Comparison with spectrophotometric method)	F	—	722
Various	—	Fertilizers, feeds	—	A	L	(Modification of official AAS method)	F	—	954
Various	—	Soils	Trace levels	A	L	Treat soil with CCl ₄ , centrifuge and collect aqueous soil extract layer	Graphite furnace	1147	
Various (7)	—	Leaf tissue	—	A	L	Comparison of (a) Dry-ashing at 500°C and (b) wet-ashing with HNO ₃ /HClO ₄ (for Ca, Cu, Fe, Mg, Mn, K, Zn)	F	—	1181
Various (14)	—	Leaf tissue	—	E	L	Dry-ash and dissolve, with addition of Li buffer (Inter-laboratory study)	S	Rotrode	1182
Various (6)	—	Orchard leaves	ng/g levels	A	L, G	Dry-ash at 500°C with Mg(NO ₃) ₂ , Dissolve and add NaBH ₄ to generate volatile hydrides of As, Sb, Bi, Ge, Se, Te	F	H ₂ /N ₂ /air	1217
Various (6)	—	Orchard leaves	µg/g levels	A	L	Digest with HNO ₃ /HClO ₄ (Cd, Fe, Cu, Mn, Cr) or dry-ash at 400°C and extract with HNO ₃ (Pb)	Graphite furnace (CRA-63)	1218	

TABLE 2.6 SOILS, PLANTS, FERTILIZERS — continued

Element	λ/nm	Matrix	Concentration	Tech.	Analyte form	Sample treatment	Atomization	Ref.
Various (9)	—	Plants, soils, waters	All levels	E, A	L	—	F Air/propane Air/ C_2H_2	1258
Various (10)	—	Soil extracts	Trace levels	A	L	Use standard addition method	Graphite furnace	1341
Various (7)	—	Corn, soils, sludges	Trace levels	A	L, G	Digest with $HNO_3/HClO_4/HF/HCl$. For Hg, reduce with $SnCl_2$	F — Cold vapour (Hg)	1407
Various (6)	—	Broccoli plants	—	A, E	L	Ash at 525°C and dissolve in HCl (1:1) (AAS—Ca, Cu, Mg, Mn; FES—Na, K)	F —	1415
Various	—	Sweet orange cultures and foliage	—	A, E	L	Digest with $HNO_3/HClO_4$	F —	1417
Various (12)	—	Spruce needles	—	A	L	Digest with $HNO_3/HClO_4$ (4:1), evaporate to low bulk, dilute and add $LaCl_3$ (for Ca)	F —	1419
Various (6)	—	Plants	—	A, E	L	Dry-ash at 400–500°C and extract ($\times 2$) with 6 N HCl (AAS—Fe, Mg, Mn; FES—Ca, K, Na)	F —	1421
Various (8)	—	Plants, soils	—	A	L	(a) Wet-digest for Cu, Zn, Mn, Mg, Fe (b) dry-ash for Ca, Mg, K	F —	1424
Various (9)	—	Pine trees	—	E, A	L	Dry-ash at 480°C, dissolve in HNO_3/HCl and dilute	F —	1425
Various (6)	—	Soils	—	A	L	Heat, mix with H_2O , allow to stand, leach with $H_2O + 1\text{ N } NH_4$ acetate	F —	1426
Various (5)	—	Soils	—	A	L	Extract with 0.5 N NaOH, centrifuge, acidity to pH 2 with 6 N HCl, centrifuge, lyophilize, dry, shake with methanol, filter, concentrate, lyophilize, dissolve in H_2O , dialyze against H_2O , dry, ash at 750°C, fuse with Na_2CO_3 in Pt, dissolve in H_2O and acidify	F —	1428
Various (6)	—	Soils	—	A, E	L	Extract with H_2O or 1 N NH_4 acetate at pH 7 (1:25 soil/extractant ratio) or extract with 1 N HCl (1:50 ratio)	F —	1429
Various (7)	—	White clover, fertilizers	—	E	S	Dry-ash in Pt at 500°C. Mix ash with graphite powder + Ag internal standard	A D.C. arc	1444
Various	—	Plant tissue	—	E	S	—	P ICP	1454

Various (8)	—	Plants	Various levels	E	S	Mix ash with graphite and form into roirode disc. Add K_2SO_4 + Na_2CO_3 (buffers) and Li^+ + Cr (internal standards)	S	Rotrode	1486
Various (7)	—	Soils	Trace levels	E	L	Treat with 6 M HCl after removal of Si by HF digestion	S, A	—	1490
Various (10)	—	Soils and soil extracts	Trace levels	E	S	Grind and mix with $CaCO_3$ or $BaCO_3$ + Cu powder. Form into briquettes	A	—	1512
Various	—	Foliage	—	E	S	Dry at 80°C, ash at 450°C, dilute with graphite + cellulose + KCl (buffer) + GeO_2 (internal standard). Form into pellets	S	—	1524