

## 4.1 CHEMICALS

### 4.1.1 Petroleum and Petroleum Products

Publications dealing with the analysis of lubricating oils still dominate this field of interest. Wear metals receive particular attention. One review paper (801) has appeared dealing with applications of AAS and related techniques to petroleum and petroleum products.

#### 4.1.1.1 Petroleum

The use of "Simplex" optimization for ICP-OES applications in oil analysis was demonstrated by Brocas (1416). Plasma power, observation height and three gas flows were the variables. The results were applied for four different solvents. Kerosene proved to be the best solvent with respect to detection limits and these were listed, together with wavelengths, for 13 elements. Wallace and Ediger (1612) described the "optimization" of ICP parameters for the determination of S in oils. They concluded that best results were obtained at 180.73 nm, using xylene as solvent and an incident r.f. power level of 1250 W.

The analysis of shale oil and related samples has received attention. The use of ETA-AAS for the determination of As in these materials was investigated by Fabec (2229). Results were compared to XRF and NAA data and excellent precision and accuracy claimed. As an aid to the isolation of metallic complexes in shale oil and shale oil retort waters, Olsen et al. (740) applied DCP-OES to the determination of B, Cu, Fe, Mo, Ni and Zn. Further work was reported by Girvin et al. (352) on the use of Zeeman AAS for the determination of Hg in oil shale off-gases (see ARAAS, 1980, 10, 110).

#### 4.1.1.2 Lubricating Oils

Kauffman et al. (957) presented a particle size independent method for the determination of Al, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Se, Sn, Ti and Zn in lubricating oils and hydraulic fluids. Metal particulates in oils were treated with an acid mixture ( $\text{HF}/\text{HNO}_3/\text{HCl}$ ) and the elements determined by DCP-OES. For the determination of Pb in used engine oils, Palmer and Rush (1542) recommended dissolution of the Pb particulates in the oil with HCl and addition of a liquid anion exchanger (Aliquat 336) in MIBK prior to analysis by FAAS. The method produced slightly higher results than a wet chemical procedure but this was thought to be due to losses during ashing in the latter method. Kaegler and Jantzen (1068) demonstrated that, for suspensions with particles of less than  $1\mu\text{m}$  diameter, a direct FAAS method gave acceptable results for Fe. With larger particle sizes, recovery of Fe was drastically reduced compared to an ashing procedure.

The use of kerosene as a solvent for lubricating oil analysis by FAAS, using the air/ $\text{C}_2\text{H}_2$  flame, was advanced by Deal and Honaker (C100). For additive

elements such as Zn, advantages such as reduced sample preparation time and lower toxicity compared to xylene and MIBK were claimed. Algeo *et al.* (1986) described the direct determination of metals in lubricating oils by ICP-OES, without dilution or pretreatment. This was achieved, it was claimed, by addition of a sample heater to a modified Babington nebulizer.

Two papers compared the use of XRF for the determination of wear metals in lubricating oils with AAS (349) and AAS and OES (C281). In both cases advantages were claimed for XRF over AAS/OES.

#### 4.1.1.3 Gasoline

The Institute of Petroleum standard titrimetric method for the determination of Pb in gasoline was modified by Frigerio *et al.* (2220) to allow the use of a FAAS finish. After extraction into aqueous ICl and digestion with  $\text{HNO}_3$ , the Pb was determined in an air/ $\text{C}_2\text{H}_2$  flame at 283.3 nm. The method permitted the use of aqueous standards, and had the advantage of considerable time saving over the standard method. In another application of an emulsion formation technique (see ARAAS, 1981, 11, 112) De La Guardia Cirugeda and Sanchez (389) described the determination of the anti-knock additive, methylcyclopentadienylmanganesetri-carbonyl, in gasoline. Samples were treated with  $\text{Br}_2/\text{CCl}_4$  and, after evaporation of excess  $\text{Br}_2$ , an anionic detergent was added to produce an emulsion. Manganese was determined at 279.5 nm by AAS in an air/ $\text{C}_2\text{H}_2$  flame. Estes *et al.* (1193) investigated the use of coupled capillary column GC-MIP for the speciation of tetraalkyl organometallics, including tetraalkyl-lead compounds, in gasolines.

### 4.1.2 Chemicals and Miscellaneous Applications

#### 4.1.2.1 Atomic Absorption Methods

Optimization of the FAAS determination of Sb in organoantimony compounds was described by Marr *et al.* (1557). Effects of flame stoichiometry in both air/ $\text{C}_2\text{H}_2$  and air/ $\text{H}_2$  flames were assessed, as were solvent effects. Ten organo-antimony compounds were successfully analysed, the results agreeing well with theoretical values.

Marr and Anwar investigated the determination of Sn in the air/ $\text{H}_2$  flame. The effects of various organic solvents were studied (1608) and Sn was determined in organotin compounds (1536) and poly(vinyl chloride)(1385).

Methods for the determination of Gd in nuclear fuels were reviewed by Coerdts *et al.* (1792). Taddia (1602) described an ETA-AAS procedure for the determination of Al in silicon, with a limit of detection of  $1.2 \text{ pg g}^{-1}$ . The determination of the matrix elements and trace components in vanadium and niobium borides was investigated by Nakamura *et al.* (1922). Samples were dissolved in  $\text{HF}/\text{H}_2\text{SO}_4/\text{HNO}_3$  acid mixtures prior to FAAS analysis.

Three methods, FAAS, polarography and spectrophotometry, were compared for

the determination of Pb in dyes and cosmetics (1833). The FAAS method was deemed most suitable. For the determination of Hg in wastes, cold-vapour AAS, potentiometric titration and spectrophotometry were compared (1832). The potentiometric titration with dithiooxamide was claimed to have economic advantages and adequate sensitivity.

#### 4.1.2.2. Atomic Emission Methods

The determination of Ag, Al, Co, Cr, Cu, Fe, In, Mn, Ni, Pb and Zn in doped cadmium mercury telluride by ETA-ICP was described by Cope *et al.* (1562). A graphite rod was used to vaporize the sample into the plasma injector gas. Karpel and co-workers (527) investigated the concentration profiles of Fe, Ga, Gd, Sm and Y in epitaxial ferrite-garnet films by spark discharge-OES, using a rotating graphite-disc electrode. Layer-by-layer etching of the films was achieved using  $H_2SO_4$ , and internal standards were added prior to analysis. Impurity concentration profiles in gallium arsenide were determined by Apuzzo (669) using glow discharge-OES. Intensities of implanted impurities were monitored as a function of time.

A comparison of the merits and disadvantages of ICP-OES, FAAS and ETA-AAS, for the determination of a number of elements in concentrated (7M) solutions of zinc chloride and potassium hydroxide, was undertaken by Greetham and Skidmore (C295). Electrothermal atomization-AAS was claimed to be particularly subject to loss of sensitivity at high electrolyte concentrations. Ehrlich *et al.* (518) compared arc and spark-OES with SSMS on a large number of different sample matrices. They concluded that SSMS was more universally applicable.

Using an atmospheric pressure He MIP, Carnahan and Caruso (1584) determined the fire retardant, tris-(2,3 dibromopropyl) phosphate, in garments, by measurement of the Br emission at 478.6 nm. Samples were vaporized electrothermally and swept into the plasma in a He gas stream.

Loree and Radziemski (1208) demonstrated the utility of Laser Induced Break-down Spectroscopy (LIBS) by determining K and Na in coal combustor product streams and Be in air. Atomic emission was monitored from the breakdown plasma in situ or in time resolved mode (TRELBS).

#### 4.1.2.3 Indirect Methods

This year has seen a resurgence of interest in indirect determinations, especially of organic compounds. Kidani (463) has reviewed applications of AAS for the analysis of medical drugs by metal complex formation. The determination of L-ascorbic acid was accomplished by following its reduction of Cu(II) to the Cu(I) neocuproine chelate, extraction of the Cu(I) complex and determination of Cu by FAAS (355). Hassan and Eldesouki (356) described the analysis of pharmaceutical preparations for sulphonamides by determination of excess Ag and Cu, using FAAS,

after metal sulphonamide production. Minami *et al.* (456) investigated the determination of alkaloids (strychnine, quinine, etc) by complex formation with Reinecke salt, with subsequent determination of the Cr content by FAAS in an air/C<sub>2</sub>H<sub>2</sub> flame. Two further papers by the same authors described the determination of low molecular weight ketones and aldehydes (461) and 2-amino-2-deoxyhexoses (476).

A method for the determination of low levels of anionic surfactants in waters was proposed by Adachi and Kobayashi (1705). The surfactant was reacted with bis-(2-(5-chloro-2-pyridylazo)-5-diethylaminophenolate) cobalt chloride, the complex extracted into benzene and the Co determined by FAAS.

#### 4.1.2.4 Sample Preparation

An interesting procedure for the determination of B in nuclear fuel reprocessing plant streams was described by Siemer (1752). Fluoride was complexed with AlCl<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, MeOH was added to form the volatile trimethylboron ester which was then aspirated into an air/C<sub>2</sub>H<sub>2</sub> flame where the molecular emission at 548 nm was monitored. For the determination of 28 elements in enriched uranium solutions, Capdevila and Roca (1775) suggested the removal of uranium as the trioctylamine complex and measurement of the remaining elements by spark source-OES.

Whitely and Merrill (1163) described a method for the determination of traces of Cr(III) in chromates, by ICP-OES. The Cr(III) was selectively chelated with 2-thenyltrifluoroacetone and extracted into xylene. The analysis of polymer-supported catalysts and organorhodium complexes was reported by Hartley *et al.* (2002). Organic material was destroyed using H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, then La(NO<sub>3</sub>)<sub>3</sub> added and the solution aspirated into an air/C<sub>2</sub>H<sub>2</sub> flame. Standards were prepared by oxidising RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> in a similar manner, thus avoiding the problems of chloride interference from commercial rhodium trichloride standards.

Table 4.1.A PETROLEUM AND PETROLEUM PRODUCTS

Element	$\lambda$ , nm	Matrix	Concentration	Technique, Atomization, Analyze Form	Sample treatment	Ref.
Ag	—	Phosphoric acid, phosphates	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Neutralize solution with NH <sub>4</sub> OH to 60°C, mix with ZnS suspension, filter, dissolve solids in 0.1 N HCl, evaporate and dilute	1651
Ag	328.068	Chemical — photographic solns.	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	—	1754
Al	309.3	Silicon	9–700 µg/g	A, ETA, L	Sample decomposed with HF and HNO <sub>3</sub>	1602
Al	309.3	Fuel oil	—	A, F, C <sub>2</sub> H <sub>2</sub> /N <sub>2</sub> O, L	Sample burnt, ashed and ash dissolved in HCl and dilute HF	1849
As	—	Petroleum	10–1000 ppb	A, ETA, L	Sample burnt in O-bomb fitted with quartz cup, products absorbed in Mg(NO <sub>3</sub> ) <sub>2</sub> –HNO <sub>3</sub>	1726
As	—	Shale oil	—	A, ETA, L	Direct determination using standards in a tetrafluran solvent system	2229
Ba	—	Oil additive	—	A, F, N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub> , L	Effect of Ca <sup>2+</sup> , Zn <sup>2+</sup> , Cl <sup>–</sup> and SO <sub>4</sub> <sup>2–</sup> on Ba signal; KNO <sub>3</sub> better	739
Ba	553.6	PVC	—	A, F, N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub> , L	—	1629
Ca	422.7	PVC	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	—	1629
Ca	—	Feeds	—	A, —, —	Digest with HCl	1785
Cd	—	Phosphoric acid, phosphates	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	See Ag, ref. 1651	1651
Cd	—	Sugar	—	A, —, —	Iodide–MIBK extraction	1891
Co	240.7	Water	—	A, —, L	1 ml of m-bis-[2(5-chloro-2-pyridylazo-S-diethyl-aminophenolato)] cobalt (III) chloride added to sample, 5 ml benzene added and organic phase analysed	1705, 1722
Cr	—	Lubricating oils	—	A, —, —	Continuous monitoring of machine part wear	663
Cr	283.56	High purity As	—	E, A, D.c., S	Sample mixed with C in silica boat, heated in silica tube to 230°C in air to remove As	1667
Cu	—	Lubricating oils	—	A, —, —	XRF comparison study indicated abnormal wear earlier than AA determinations	349
Cu	324.8	Crude oils	10–105 mg/g	A, ETA, L	Loss of Cu prevented by adding Mg(NO <sub>3</sub> ) <sub>2</sub>	479
Cu	—	Lubricating oils	—	A, —, —	See Cr, ref. 663	663
Cu	—	Lubricating oils	—	A, ETA, L E, A in F, L	Dilute with MIBK or xylene, ash	802
Cu	—	Edible oils	5 ppb	E, P, L	—	1029

Cu	324.7	Petroleum	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Detection affected by matrix interferences of the fractions and by the form of Fe in the sample See Ag, ref. 1651	1538, 1949 1651
Cu	—	Phosphoric acid, phosphates	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L		
Cu	—	Feeds	—	A, —, L	Digest HNO <sub>3</sub> and perchlorate	1763
Cu	—	Sugars	—	A, —, —	See Cd, ref. 1891	1891
Cu	—	pH standard reference materials	0.01–0.2 µg/g	A, —, —	Extraction with bathocuproine in presence of NH <sub>4</sub> OH at pH 4.3–6.0	2004
Fe	—	Lubricating oils	—	A, —, —	See Cu, ref. 349	349
Fe	—	Lubricating oils	—	A, —, —	See Cu, ref. 663	663
Fe	—	Lubricating oils	—	A, ETA, L E, A in F, L	See Cu, ref. 802	802
Fe	—	Petroleum	8.1 ppm	A, —, L	Study of trace elements after vacuum distillation into 3 fractions	845
Fe	—	Lubricating oils	—	A, —, L	Direct determination of Fe more dependent on particle size than indirect colorimetric method	1068
Fe	248.3	Petroleum	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	See Cu, Ref. 1538	1538
Fe	—	Feeds	—	A, —, L	See Cu, ref. 1763	1763
Gd	—	Nuclear fuels	—	E, A, P, — A, ETA, —	Review of emission and AA techniques	1792
Ge	—	Gasoline	—	E, P, G	Gas-chromatographic separation	1193
Hg	253.7	Oil shale gases	5–250 ppb	A, ETA, G	Continuous monitoring of Hg in gas streams; Zeeman background correction	352
Hg	253.7	Pharmaceuticals	—	A, ETA, S or L	Hg extracted with dithizone into chloroform	1559
Hg	—	Paint	—	A, —, G	Digested with acidic KMnO <sub>4</sub> or HNO <sub>3</sub> in bomb at 140°C; Hg determined by AA with cold vapour atomization	1847
Hg	—	Drugs	—	A, —, G	Decomposition apparatus for pyrolysis of samples in Ar and combustion of the pyrolysis products in O <sub>2</sub> with amalgamation of Hg on Ag wool, followed by liberation at high temperature and determination by AA	1859
Mn	279.6	Gasoline	0–5 mg/l	A, F, L	10 ml petroleum + 15 ml 1:1 Br <sub>2</sub> /CCl <sub>4</sub> , evap. excess Br <sub>2</sub> , add antonic emulsifier, dilute with H <sub>2</sub> O	389
Mn	—	Feeds	—	A, —, L	See Cu, ref. 1763	1763
Na	—	Crude and heavy oils	0–50 ppm	A or E, —, L	Comparison of flame photometric results with ashing–AAS and rotating disc emission techniques	1615
Nb	—	C and SiO <sub>2</sub> matrices	—	E, A, D.c., S	LiF and C + AgNO <sub>3</sub> as thermochemical reagents	1865

Table 4.1A PETROLEUM AND PETROLEUM PRODUCTS—continued

Element	$\lambda/\text{nm}$	Matrix	Concentration	Technique, Atomization, Analyze Form	Sample treatment	Ref.
Ni	—	Petroleum	28–84 ppm	A, —, —	—	803
Ni	—	Petroleum	25.5 ppm	A, —, L	—	845
Ni	—	Petroleum	—	E, P, L	—	C1247
Ni	305.08	High purity As	—	E, A, D.c., S	See Cr, ref. 1667	1667
Ni	232.0	Gas oil	—	A, ETA, L	Sample dissolved in xylene, dried at 140°C, calcined at 900°C, atomized at 2600°C	1737
P	—	Edible oils	0.5 ppb	E, P, L	—	1029
Pb	—	Oils	—	A, —, —	See Cu, ref. 663	663
Pb	—	Gasoline	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Automated dilution with MIBK stabilization of Pb alkyls by I <sub>2</sub> and Aliquat 386 addition	738
Pb	—	Gasoline	—	E, P, G	See Ge, ref. 1193	1193
Pb	261.4	Used engine oils	0.1–2.5% m/n	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Dissolve lead particulates in oil with HCl and liquid ion-exchanger in MIBK	1542
Pb	—	Phosphoric acid phosphates	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	See Ag, ref. 1651	1651
Pb	283.3	Additives and gear oil	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Sample dissolved in 15 ml xylene; sample diluent prepared by dissolving 0.1 g Zn dialkylphosphorodithionate in 500 ml of xylene add 7 ml of acetic acid and dilute to 1 l with xylene	1656
Pb	283.08	High purity As	—	E, A, D.c., S	See Cr, ref. 1667	1667
Pb	—	Cosmetic dyes	—	A, —, —	Comparison of dithizone method, polarography and AA	1833
Pb	—	Sugar	—	A, —, —	See Cd, ref. 1891	1891
Pb	283.3	Food packaging, paper and cardboard	—	A, ETA, —	Pb extracted with 3% HOAc	1948
Pb	283.3	Petrol	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Extracted with HCl, converted to PbNO <sub>3</sub> by digestion with HNO <sub>3</sub>	2220
Pd	—	Catalysts	0.1–0.5%	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	—	1869
Rh	—	Organo-rhodium	0–20 ppm	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Organic material destroyed with H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub> , LaNO <sub>3</sub> added	2002
S	—	Petroleum	—	E, P, L	—	C1247
S	—	Oils	—	F, P, L	Xylene used as diluent	1612
Sb	—	Organo-antimony	—	A, F, Air/H <sub>2</sub> , Air/C <sub>2</sub> H <sub>2</sub> , L	Dissolve sample in suitable organic solvent, make 5% in HCl, add 35 ml ethanol	1557

Si	—	Gasoline coker naphthas	1–30 ppm	E, P, D.c., L	710
Si	—	GaAs	—	A, ETA, L	1813
Si	251.6	Fuel oil	—	A, F, C <sub>2</sub> H <sub>2</sub> /N <sub>2</sub> O, L	1849
Sn	—	Gasoline	—	E, P, G	1193
Sn	286.5 284	Various	—	A, F, Air/H <sub>2</sub> , L E, F, Air/H <sub>2</sub> , L	1536
Sn	—	—	—	A, F, Air/H <sub>2</sub> , L	1608
Ta	—	C and SiO <sub>2</sub> matrices	—	E, A, D.c., S	1865
V	—	Petroleum	1.8–130 ppm	A, —, —	803
V	—	Petroleum	92 ppm	A, —, L	845
V	—	Crude oil	—	A, F, L	1034
V	—	Petroleum	—	E, P, L	C1247
Zn	—	Lubricating oil	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	C100
Zn	—	Feeds	—	A, —, L	1763
Various	—	Petroleum products	Trace levels	E, P, D.c., L	C227
Various	—	Lubricating oils	10–500 ppm	E, —, — A, —, —	C281
Various	—	Oil, fats	µg/g	A, ETA, L	398
Various	—	Crude oils	—	A, ETA, L	526
Various	—	Menhaden oil	—	A, ETA, L	736
Various	—	Shale oil, shale oil retort waters	Trace levels	E, P, D.c., L	740
Various	—	Oils, etc.	—	A, —, —	801
Various	—	Lubricating oil, hydraulic fluids	—	E, P, D.c., L A, F, L	957
Various	—	Oil	—	E, P, L	1416



Table 4.1A PETROLEUM AND PETROLEUM PRODUCTS—continued

Element	$\lambda/\text{nm}$	Matrix	Concentration	Technique, Atomization, Analyte Form	Sample treatment	Ref.
Various (15)	—	Oil	—	E, P, L	Oil sample dissolved in organic solvent (Ag, Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Ti, V, Zn)	C1685
Various (5)	—	Lubricating oils	—	A, F, Al/C <sub>2</sub> H <sub>2</sub> , L	Sample dissolved in mixture of HOAc—PhMe solvent (Cr, Cu, Fe, Li, Pb)	1827
Various	—	Lubricating oils	—	E, P, D.c., L	Direct nebulization using heated Babington principle nebulizer	C2162
Various	—	Lubricating oils	—	E, A, D.c., L	Investigation into use of rotating disc electrode	C2165

Table 4.1B CHEMICALS AND MISCELLANEOUS MATERIALS

Element	$\lambda/\text{nm}$	Matrix	Concentration	Technique, Atomization, Analyte Form	Sample Treatment	Ref.
Ag	—	Pharmaceutical products	—	A, —, —	Measurement of excess Ag ions after metal-sulphonamide reaction	356
Al	—	Gallium arsenide	—	A, F, S	Dissolve in HCl/HNO <sub>3</sub> , ash at 1000–1350°C	1174
As	—	Ammonium paratungstate	< 1 ppb	E, P, D.c., L	Dissolve APT in NaOH	C232
As	—	Dental alloys, acrylic resins	—	A, —, L	Hygienic chemical studies on dental materials, resin samples dipped in 4% AcOH at 60°C	1040
Au	267.5 or 242.7	10 elements	0.05–2 ppm	E, A, L	Concentration by mixing suitable solvents of diantipyrinylmethane extracted into bis(2-chloroethyl)ether, light petroleum added and organic phase applied to graphite electrode. Excited in a 8 A.c.c arc	580
Au	—	Precious-metal catalyst	—	E, P, D.c., L	After fire assay, bead dissolved in aqua regia	C2152
B	—	Ammonium paratungstate	< 1 ppb	E, P, D.c., L	See As, ref. C232	C232
Ba	—	Bullet residue, primer particles	—	A, F, —	—	947
Ba	—	Organic solvents	1 ppm	A, E.T.A., — E, F, L	Indirect method for S, oxidize with NaBH <sub>4</sub> in presence of NaOH Ba compounds with H <sub>2</sub> SO <sub>4</sub> , ppt. as Ba; excess Ba determined	981
Ca	—	Brines	—	A, —, S	—	789
Ca	—	Ag catalysts	—	A, F, Atr/C <sub>2</sub> H <sub>2</sub> , L	Dissolved in HNO <sub>3</sub> , 3% LaNO <sub>3</sub> added	824
Ca	—	Sodium chloride	—	A, —, L	Separation on chelating resin, Ca eluted with 2N HNO <sub>3</sub>	910
Ca	—	Ni(OH) <sub>2</sub> , NiSO <sub>4</sub>	—	F, —, Atr/C <sub>3</sub> H <sub>8</sub> , L	—	1213
Cd	—	Ag catalysts	—	A, F, Atr/C <sub>2</sub> H <sub>2</sub> , L	See Ca, ref. 824	824
Cd	—	Dental alloys, acrylic resins	3.5 ppm–10%	A, —, —	See As, ref. 1040	1040
Cd	—	Ceramic, enamel ware	—	A, —, L	Leach in 4% HAc	C2337
Cl	—	Semiconductor crystals	—	A, —, L	Dissolve in HNO <sub>3</sub> containing AgNO <sub>3</sub> and Ba(NO <sub>3</sub> ) <sub>2</sub> , add Na <sub>2</sub> SO <sub>4</sub> solution, adjust pH to 2, filter BaSO <sub>4</sub> + AgCl, determine Ag or Ba in filtrate	1810
Co	240.7	Hexamines	0.02–0.70 mg	A, F, Atr/C <sub>2</sub> H <sub>2</sub> , L	Mix with 1 ml pyridoxal hydrochloride soln, 0.5 ml pyridine and 1 ml MeOH, add CO <sub>2</sub> , Cl <sub>2</sub> soln and 0.2 ml N NaOH	476
Co	—	Ni–Co–P coatings	—	E, —, L	Layer dissolved in HNO <sub>3</sub>	547

Table 4.1B CHEMICALS AND MISCELLANEOUS MATERIALS—continued

Element	$\lambda/\text{nm}$	Matrix	Concentration	Technique, Atomization, Analyte Form	Sample Treatment	Ref.
Cr	4254	$\text{Si}_3\text{N}_4$	1–5 ppm	E, P, D.c., L	Fuse in 90/10 $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ , extract in $\text{H}_2\text{O}$	C232
Cr	357.87	Alkaloids	0.03–2.00 as alkaloids	A, F, Air/ $\text{C}_2\text{H}_5$ , L	Add 1 ml of Reinecke salt soln. to sample soln.; dehydrate phase.	456
Cr	—	Gallium arsenide	0.1 mg/g to 3 $\mu\text{g/g}$	A, ETA, L	—	992
Cr	—	$\text{Ca/Co CrO}_4$ , thermal battery	—	E, P, ICP, S	$\text{CaCrO}_4$ mixed with KCL/LICI eutectic pressed into wafer containing silica binder. Also used for Cr in $\text{B/CaCrO}_4$ pyroelectric mixes.	1163
Cs	—	Ag catalysts	—	A, F, Air/ $\text{C}_2\text{H}_5$ , L	See Ca, ref. 824	824
Cu	—	Ascorbic acid	—	A, —, —	Determined after reduction of $\text{Cu}^{2+}$ —neocuproine chelate to $\text{Cu}^+$ —neocuproine chelate, extract in $\text{CHCl}_3$	355
Cu	—	Pharmaceutical products	—	A, —, —	See Ag, ref. 356	356
Cu	324.7	Ketones and aldehydes	0.01–2 mg	A, F, Air/ $\text{C}_2\text{H}_5$ , L	Add to 1 ml solution, 2 ml thiosemicarbazide solution, 1 ml $\text{Cu}(\text{Ac})_2$ , extract $\text{C}_6\text{H}_6$ , dehydrate $\text{C}_6\text{H}_6$ phase, dilute with EtOH	461
Cu	324.8	$\text{H}_2\text{SO}_4$	0.02 ppm	A, F, Air/ $\text{C}_2\text{H}_5$ , L	50 g sample evaporated to dryness, residue dissolved in 3 ml (1:1), dilute with 2 ml water.	489
Cu	—	Ni—Cu—P coatings	—	E, —, L	See Co, ref. 547	547
Cu	—	Antifouling paints	30.2–48.9%	A, —, L	Decompose in 3:1 $\text{HNO}_3/\text{H}_2\text{SO}_4$ , filter, dilute with 1N HCl	610
Fe	374.8	$\text{Si}_3\text{N}_4$	1–50 ppm	E, P, D.c., L	See Cr, ref. C232	C232
Fe	—	PVC	—	A, —, L	Dissolve in THF or DMF, treat with 1:1 $\text{H}_2\text{SO}_4/\text{HClO}_4$	348
Fe	—	Ferrite-garnet	17%	E, S, L	Film etched with 5 ml $\text{H}_2\text{SO}_4$ , diluted with 1 ml $\text{H}_2\text{O}$ , 1 ml internal standard of 0.17 mg La, Co, and In added, 0.5 ml of this solution introduced into spark discharge (3 A) using rotating electrode	527
Fe	—	Ag catalysts	—	A, F, Air/ $\text{C}_2\text{H}_5$ , L	See Ca, ref. 824	824
Ge	—	GaAs	—	E, glow discharge, S	Samples sputtered in low pressure Ar discharge	669
Ge	—	Herbal drugs	65–98 $\mu\text{g/g}$	A, ETA, L	Study of various solvents for extraction of Ge	772
Ge	—	—	—	A, ETA, L	—	C2373
Hg	—	Pharmaceuticals	3–250 ng/g	A, F, L	—	2035
Mg	—	Brines	—	A, —, S	—	789
Mg	—	Siloxane coatings	—	A, —, —	AAS used after electric discharge techniques	955

Mg	—	Ni(OH) <sub>2</sub> , NiSO <sub>4</sub>	—	F, —, Alr/C <sub>3</sub> H <sub>8</sub> , L	—	1213
Mo	3798	Si <sub>3</sub> F <sub>8</sub>	10–50 ppm	E.P. D.c., L	See As ref. C232	C232
Na	—	Sodium hydroxide	—	A, —, L	NaCl determined by indirect method. Neutralize, acidify solution with HNO <sub>3</sub> , ppt. Cl <sup>-</sup> with AgNO <sub>3</sub> solution, measure excess Ag	1103
Ni	—	Ni–Co–P, Ni–Cu–P coatings	—	E, —, L	See Co. ref. 547	547
Os	—	Spent catalysts	—	A, F, Alr/C <sub>2</sub> H <sub>4</sub> , L	—	1107
P	—	Ammonium paratungstate.	—	E.P. D.c., L	See As. ref. C232	C232
P	—	Ni–Co–P, Ni–Cu–P coatings	—	E, —, L	See Co. ref. 547	547
Pb	217.0	H <sub>2</sub> SO <sub>4</sub>	0.05 ppm	A, F, Alr/C <sub>2</sub> H <sub>4</sub> , L	See Cu. ref. 489	489
Pb	—	Paint	—	E, —, —	Direct-reading technique	954
Pb	—	Paint	—	A, F or ETA, —, L	AOAC method used, samples wet-washed using HNO <sub>3</sub>	1033
Pb	—	Dental alloys, acrylic resins	—	A, —, L	See Cd. ref. 1040	1040
Pb	—	Paint	—	A, F, L	Dry ash at 300°C, dissolve residue in HNO <sub>3</sub>	1192
Pb	283.3, 217.0	Paint	—	A, F, Alr/C <sub>2</sub> H <sub>4</sub> or Alr/H <sub>2</sub> , L	HNO <sub>3</sub> treatment	2024
Pb	—	Ceramic, enamel ware	—	A, —, L	See Cd. ref. C2337	C2337
Pb	—	Aluminosilicate catalyst	—	A, —, L	Si removed by HF	662
Sb	—	Bullet residue, primer particles	—	A, F, —	—	947
Se	196.0	H <sub>2</sub> SO <sub>4</sub>	—	A, F, G	Hydride generation technique does not work	2267
Si	251.6	Silicon tetrachloride	—	A, ETA, G	ETA used as detector after GLC	533
Si	251.6	High-purity graphite.	—	F, P, D.c., L	Ashed at 800°C for 12 h, dissolve residue in 3:1 HCl/HNO <sub>3</sub> , Solution adjusted to desired pH, treated with chelating resin, trace elements determined after HNO <sub>3</sub> digestion of resin	C2436
Sn	—	Antifouling paints	0.52–9.30%	A, —, L	See Cu. ref. 610	610
Sn	—	Siloxane coatings	—	A, —, —	See Mg. ref. 955	955
Sn	224.6	PVC	5–20 µg/ml	A, F, Alr/H <sub>2</sub> , L	Digest in 1 ml H <sub>2</sub> SO <sub>4</sub> , 2 ml 50% H <sub>2</sub> O <sub>2</sub> , dilute to 25 ml with water	1355

Table 4.1B CHEMICALS AND MISCELLANEOUS MATERIALS—continued

Element	$\lambda/\text{nm}$	Matrix	Concentration	Technique, Atomization, Analyte Form	Sample Treatment	Ref.
Sn	—	—	—	A, ETA, —, L	—	C2373
Ti	276.7	10 elements	—	E, A, L	See Au, ref. 580	580
Zn	—	Varnish	—	A, —, —	Ash scrapings	661
Zr	—	Catalytic compounds	—	A, F, L	HF/HNO <sub>3</sub> /HCl dissolution	2279
—	—	Nitric acid, tri-n-butyl phosphate	—	E, P, D.c., L	—	C2459
Various (9)	—	Polysaccharides	0.25–2.0 ppm	E, P, S	Sample preparation method using special digestion apparatus (Ag, As, Bi, Cd, Cu, Hg, Pb, Sb, Sn)	4
Various (11)	—	NaClO <sub>4</sub>	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> or ETA, L or S	Adjust pH, filter through activated charcoal, dissolve absorbed metals in HNO <sub>3</sub> (Ag, Bi, Co, Cu, Cd, Fe, In, Mn, Ni, Pb). For Hg the charcoal is heated directly in the ETA	123
Various (11)	—	Fatty acid residues	—	E, P, D.c., L	(Ca, Cd, Cu, Fe, Mg, Ni, Zn)	C228
Various	—	Printed wiring boards	—	E, P, D.c., G	Hydride generation (As, Pb, Sb, Hg)	C233
Various	—	ZnCl <sub>2</sub> , KOH	—	A, ETA or P, D.c., L	Use of ICP 5000 and HGA 500 ETA	C295
Various (9)	—	InSb	—	—	Study of various techniques	333
Various (12)	—	CaWO <sub>4</sub>	5–250 ppm	A or E, ETA, L	Sample dissolved in HF (Be, Cd, Gd, Ge, Mg, Pb, Zn, Te, Zn)	374
Various (5)	—	Ga–Gd film	—	E, A, L	Sample mixed with graphite	527
Various (5)	—	Inorganic salts	—	A, ETA, L	Etched with H <sub>2</sub> SO <sub>4</sub> (Te, Ga, Gd, Sm, Y)	590
Various (11)	—	Zn-containing waste	mg–g	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Chromatographic separation (Cu, Fe, Ni, Pb, Zn)	727
Various (5)	—	Ferrite garnet	—	E, S, L	Bacterial leaching and separation on cellulose	883
Various (6)	—	Molybdenum (VI) compounds	—	A, F, Air/C <sub>2</sub> H <sub>2</sub> , L	Etched with H <sub>2</sub> SO <sub>4</sub> , graphite disc electrode (Cd, Fe, Ga, Sm, Y)	930
Various (6)	—	High-purity Fe, Cr, Mn	—	A, F, L	Samples complexed and extracted with DDC/MTBK (Co, Cu, Fe, Mn, Ni, Zn)	1051
Various (13)	—	Glass	—	E, A, S	Separation of trace elements from matrix by sorption of their complexes with ammonium <i>O</i> -diethyl dithiophosphate onto activated C (Bi, Cd, Cu, In, Pb, Ti)	1373

Various (9)	-	Cd, Hg, Fe	100–500 ppm	E, P, L	0.25 g sample dissolved in aqua regia (Ag, Al, Cr, Cu, Fe, In, Mn, Li, Zn)	1562
Various (6)	-	Ammonium hydrogen fluoride	-	E, -, -	(Fe, Mn, Mo, Ni, Pb, Si)	1626
Various (6)	-	In–Ga–As Ga–As–P Ga–Al–As High-grade Si	-	A, F, Al/C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub> , L	Films removed by anodic oxidation in aq. ammonium pentaborate (Al, As, Ga, In, P, Pb)	1639
Various (14)	-	Uranium solution	-	E, A, D.c., S	-	1652
Various (28)	-	Sugars	-	E, S, L	U removed by extraction with Bu <sub>3</sub> PO <sub>4</sub>	1775
Various (5)	-	SIC	-	A, -, L	Ion-exchange separation (Ca, K, Mg, Na, Si)	1890
Various (7)	-	Vanadium and niobium borides	-	A, -, L	Sample fused with Na <sub>2</sub> CO <sub>3</sub> /KNO <sub>3</sub> (4:1) (Al, Ca, Fe, Mg, Mn, Ni, Si)	1921
Various (44)	-	Ceramics	-	A, -, L	Sample treated with HF, H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> (B, Ca, Si, V, and others)	1922
Various (17)	-	H <sub>3</sub> PO <sub>4</sub> , POCl <sub>3</sub>	-	A, -, -	-	C2317
Various (7)	-	Gold liquors	-	A, ETA, L	-	C2384
	-		-	A, -, -	(Au, Cu, Fe, Li, Pb, Pd, Sn)	C2409