PART - III

TRACE DETERMINATION OF METALS IN HIGH PURITY GRADE METALS, ALLOYS, PHARMACEUTICALS AND IN THE ENVIRONMENT

CHAPTER XI

TRACE DETERMINATION OF METALS IN HIGH PURITY GRADE METALS, ALLOYS, PHARMACEUTICALS AND IN THE ENVIRONMENT

RESUME

The solvent extraction and spectrophotometric methods, developed in PART II are applied for the trace determination of selenium, tellurium, arsenic, antimony, bismuth, titanium and vanadium. in high purity grade metals, alloys, pharmaceuticals and in the environment samples viz. standard samples, blood serum, urine, soil, plant, water, industrial effluents and waste water samples collected from different areas of Baroda district. These results are also compared with those determined by atomic absorption spectrophotometry.

INTRODUCTION

The only characteristic that the trace elements have in common is that they normally occur or function in living tissues in low concentrations relative to the major elements. They vary markedly in their physicochemical properties, as well as in their biological properties, so that there is no common chemical denominator to aid the investigator. Many of the trace elements are linked by coordination or covalent bonds to organic compounds of varying size, lability, and biological potency.

Analysis of the tissues of the human body will show the presence of most of the metallic elements, in greater or lesser amounts. The soil in which plants grow contains metals from a number of sources, principally the rocks from which the soil was formed, as well as fertilisers, sewage sludge and other materials added in the course of agricultural activities. Metals are also contributed by the debris of mining and industrial waste, by the dust and smoke of fossil fuel combustion and by other forms of atmospheric pollution. Water too makes its contribution to an extent related to the source of supply and the degree of pollution.

Pharmaceutical analysis has made rapid progress in the past several decades with a large number of new reagents, new instruments and new methods. A choice between the almost innumerable methods described in the literature may be very difficult in spite of the abundance of available methods of analysis. Amongst all the methods spectrophotometry is rapid, simple, selective and sensitive. Solvent extraction is an important technique and widely used in analytical and pharmaceutical chemistry.

The solvent extraction and spectrophotometric determination of several metal ions with hydroxamic acids are reported in Part II Chapters IV - X. Most of these metals are present in trace quantities in synthetic and high purity grade metals and alloys, geological samples, soils, plants, industrial effluents, blood and tissues and pharmaceuticals. With this view in the present investigation the method is further extended for the determination of selenium, tellurium, arsenic, antimony, bismuth, titanium and vanadium in standard high purity grade metals, alloys, pharmaceuticals and in the environmental samples.

EXPERIMENTAL

The details of the chemicals, glasswares, extraction procedure are essentially the same as described in Part II, Chapters IV – X of this thesis. A brief description on the sample preparation is described.

SAMPLING

The WHO method of sampling is adopted (1,2).

SAMPLE PREPARATION

The synthetic samples of steels, alloys, ores etc. were digested with conc. hydrochloric and perchloric acids. The hot solution was filtered and centrifuged off any silicious residue. The filtrate was evaporated and diluted to 100 ml with 0.1 M HCl. In case of arsenic the Lynch and Mihailou (3) procedure is used for sample preparation.

Water samples

The water samples were filtered through the Whatman filter paper No. 542 and used as such for trace metal determination.

Plant and soil samples

Depending upon the concentration of trace metals in plants or soils about 1-10 g of samples were digested with excess of hydrochloric acid and 10-20 ml of perchloric acid. The filtrate was evaporated and diluted to 100 ml with 0.01 M HCl. The appropriate aliquot of this solution was used for the determination of the trace metals.

General procedure

The procedure[1] for the determination of selenium, tellurium, arsenic, antimony, bismuth and vanadium is essentially the same as described in Part II.

RESULTS AND DISCUSSION

The environmental samples from the Nandesari and GIDC industrial areas of Baroda were collected and analysed for the trace metals.

The concentration of selenium in the high purity grade alloys and in the standard samples is given in Table 1. The selenium is also determined in lotion and data are given in Table 2. The data on the selenium in the whole blood samples and in the environmental samples viz. soil, plant and industrial effluents are given in Table 3. Similarly, the data on the determination of the tellurium are shown in Tables 4-6.

The standard samples of arsenic were analysed to check the reliability of method and these data are given in Table 7. The traces of arsenic is also determined in industrial samples of Baroda city (Table 8). The data on the determination of antimony are given in Tables 9-10. The bismuth is determined in the standard samples and values obtained are given in Table 11. The pharmaceutical samples e.g. eye drops, ointment etc. have been analysed for bismuth and these values are recorded in Table 12. The determination of bismuth in the environmental samples is given in Table 13.

TABLE 1

Determination of traces of selenium in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value selenium (%)	Selenium, found		
		Spectrophotometry (%)	Co-efficient of variation (%)	AAS (%)
	Stainless steels			
339 Cr-17 Ni9-Se02 (SAE 303 Se)	0.247	0.2464	0.28	0.2469
	Copper "Benchmark"			
393 Unalloyed Cu"O"	0.05	0.0503	0.99	0.0499
	Selenium ppm			
	Low alloy steels			
361 AISI 4340	3.16	3.19	0.31	3.17
362 AISI 94B17 (Mod)	0.95	0.96	2.11	0.94
363 Cr-V (Mod)	0.13	0.11	9.09	0.12
	Copper base-alloys			
874 Cupro-Nickel, 10% (CDA 706 High purity)	0.12	0.13	7.69	0.12
875 Cupro-Nickel, 10% (CDA 706) "Doped)	0.32	0.35	8.57	0.34

TABLE 2

Determination of selenium in the pharmaceuticals

Sample	Certified value selenium %	Selenium found, %		
		Spectrophotometry	Co-efficient of variation	AAS
Selsun blue (Abbott)	1.0	1.01	0.79	0.999
Selenium sulphide(Herbert)	2.5	2.49	0.36	2.500
Selsun (Abbott)	2.5	2.49	0.28	2.499

TABLE 3

Determination of selenium in the environment

Sample	Selenium found, ppm	
	Spectrophotometry	AAS
Soil (Nandesari, Baroda)	0.005-0.09	0.004-0.08
Soil (GIDC Baroda)	0.05 -1.01	0.05 -1.03
Plant (Nandesari, Baroda)	0.02 -5.00	0.02 -5.10
Television Tube Manufacture	0.08 -0.51	0.07 -0.53
Petrochemical effluents	0.10 -5.5	0.10 -5.8
Whole Blood	5.4 -1.72	5.0 -1.45

TABLE 4

Determination of traces of tellurium in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value tellurium (%)	Tellurium, found		
		Spectro- photometry (%)	Co-efficient of variation (%)	AAS (%)
Cast steel				
1143_a Blast-furnace(1)	0.016	0.0157	3.18	0.0161
1144_a Blask-furnace(2)	0.022	0.0223	2.69	0.0221
Copper-base alloys				
1034 Unalloyed copper	0.5	0.4999	0.08	0.4999
Copper "Benchmark"				
393 Unalloyed Cu"O"	0.5	0.4998	0.10	0.5000
398 Unalloyed CuV	11	10.9998	0.004	11.0002
Tellurium ppm Low alloy steels				
361 AISI 4340	0.77	0.75	2.67	0.76
363 Cr-V (Mod)	1.15	1.15	2.60	1.14
364 High-Carbon (Mod)	0.26	0.25	4.00	0.24

TABLE 5

Determination of tellurium in the pharmaceuticals

Sample	Certified value tellurium %	Tellurium found, %		
		Spectrophotometry	Co-efficient of variation	AAS
Tellurium oxide + Zinc oxide mixture	5.0	4.98	0.40	5.01
	10.0	10.02	0.30	9.99
	12.5	12.50	0.24	12.49
	15.0	14.75	0.27	15.01
	20.0	20.10	0.25	20.00

TABLE 6

Determination of tellurium in the environment

Sample	Tellurium found, ppm	
	Spectrophotometry	AAS
Soil (Nandesari, Baroda)	0.02 - 0.09	0.02 - 0.08
Soil (GIDC Baroda)	0.03 - 3.50	0.02 - 3.30
Plant (Nandesari, Baroda)	0.04 - 1.50	0.04 - 1.50
Petrochemical effluents	0.9 - 1.60	0.07 - 1.55
Whole blood	0.95 - 1.12	0.90 - 1.10

TABLE 7

Determination of traces of arsenic in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value arsenic (%)	Arsenic, found		
		Spectro-photometry (%)	Co-efficient of variation (%)	AAS (%)
Low alloy steels				
361 AISI 4340	0.017	0.0169	4.73	0.1699
362 AISI 94B17 (Mod)	0.092	0.0915	0.77	0.0918
363 Cr-V (Mod)	0.010	0.0985	0.81	0.0999
364 High carbon (Mod)	0.052	0.0515	1.75	0.0520
Tool steels				
50_cW 18-Cr4-VI	0.022	0.0224	3.13	0.0221
Copper "Benchmark"				
393 Unalloyed Cu"O"	0.41	0.4109	0.12	0.4099
Lead-base alloys				
1132 Bearing metal	0.057	0.0565	1.42	0.0569
Special ingot irons and low-alloy steels				
462 Low alloy B	0.046	0.0458	1.31	0.0459
Arsenic ppm				
Cast steel				
1138_a Cast steel (No.1)	3.75	3.77	1.06	3.77
1139_a Cast steel (No.2)	3.75	3.74	0.53	0.32
1143_a Blast furnace (1)	2.25	2.24	0.45	2.26
1144_a Blast furnace (2)	2.99	3.00	0.33	2.97
Copper base alloys				
874 Cupro-Nickel,10% (CDA 706 High purity)	0.45	0.47	6.67	0.44
875 Cupro-Nickel, 10% (CDA 706)"Doped"	0.75	0.73	2.74	0.75

TABLE 8

Concentration of arsenic in industrial effluents, plants and soils

	Arsenic found, (ppm)[a]	
	Present method	AAS
Soil sample	190-500	180-480
Plant sample	155-480	150-480
Cabbage	2.5-5.0	2.5-5.0
Apple	1.5-3.0	1.5-3.0
Industrial effluents	50-990	40-990
Phosphorus pentoxide	95-150	90- 150
Super phosphate	30-60	25-55
Insecticide	280-385	280-385
Sulphuric acid	18-55	20-55
Glass	1.0-35	0.5-30
Waste water	0.5-25	0.6-30

a = Average of eight determinations.

Ranges for highest and lowest concentration of arsenic.

TABLE 9

Determination of traces of antimony in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value antimony(%)	Antimony, found		
		Spectro-photometry (%)	Co-efficient of variation (%)	AAS (%)
Low alloy steels				
364 High carbon (Mod)	0.0340	0.0345	2.32	0.0341
Copper "Benchmark"				
393 Unalloyed Cu"O"	0.25	0.2506	0.32	0.2499
398 Unalloyed Cu V	7.5	7.5008	0.013	7.5001
Lead-base alloys				
1131 Solder Pb60-Sn40	0.43	0.4305	0.19	0.4299
1132 Bearing Metal	10.2	10.2000	0.002	10.2002
Antimony ppm				
Low alloy steels				
361 AISI 4340	5.11	5.13	0.39	5.12
362 AISI 94B17 (mod)	15.83	15.82	0.06	15.82
Steels (Granular form)				
101 F Stainless (AISI 304 L)	1.10	1.11	1.80	1.10
874 Cupro-Nickel,10% (CDA 706) High purity	1.22	1.21	1.65	1.21

TABLE 10

Concentration of antimony in industrial effluents, plants and soils

Sample	Antimony concentration (ppm)*	
	Present method	AAS
Soil sample	0.5-14.6	0.8-13
Plant sample	1.0-14.0	0.5-10
Orchid leaves	3.3- 6.0	3.0-5.5
Rock sample (Garnitic)	0.5- 2	0.45-3.6
Hair	0.6- 1.3	0.62-1.3
Industrial effluents		
i) Textile industries	1.0-6.0	1.0-5.5
ii) Paint industries	3 - 14	2 - 14
iii) Enamel coated container	5 - 13	5 - 10

* Average of 10 determinations.

TABLE 11

Determination of traces of bismuth in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value bismuth (%)	Bismuth, found		
		Spectrophotometry (%)	Co-efficient of variation (%)	AAS (%)
Copper "Benchmark"				
393 Unalloyed Cu"O"	0.1	0.0998	0.50	0.0999
398 Unalloyed Cu V	2.0	1.9998	0.02	2.0010
Lead-base alloys				
1131 Solder Pb60-Sn40	0.06	0.0603	0.83	0.0599
1132 Bearing metal	0.052	0.0522	0.77	0.0520
Bismuth ppm Low alloy steels				
361 AISI 4340	0.84	0.86	1.16	0.86
362 AISI 94B17 (Mod)	4.18	4.19	0.48	4.19
363 Cr-V (Mod)	0.17	0.15	6.67	0.15
364 High carbon (Mod)	1.88	1.89	0.53	1.88
Copper-base alloys				
874 Cupro-Nickel, 10% (CDA 706) High purity	0.42	0.40	7.5	0.40
875 Cupro-Nickel, 10% (CDA 706) "Doped"	6.27	6.28	0.64	6.29

TABLE 12

Determination of bismuth in pharmaceuticals

Sample	Certified value bismuth (ppm)	Bismuth, found (ppm)		
		Spectro-photometry	Co-efficient of variation	AAS
Kaodene (Pfeizer)	194.4	194.8	0.33	194.6
Pepto-Bismol	52.7	52.5	0.19	52.7
Pectomycin	5.74	5.7	0.35	5.7
	9.55	9.54	0.21	9.53

TABLE 13

Concentration of bismuth in standard samples, industrial effluents, plants and soils

Sample	Bismuth found, ppm[a]	
	Present method	AAS
NBS (1.15) sample	1.15 1.16	1.15 1.14
Soil sample	3-60	2.5-65
Industrial effluents	10-500	10-550
Plant samples	2.5-80	2.5-80

a = Average of eight determinations
Ranges for highest and lowest concentrations found.

TABLE 14

Determination of traces of titanium in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value titanium (%)	Titanium, found	
		Spectrophotometry (%)	Co-efficient of variation (%)
Low alloy steels			
361 AISI 4340	0.020	0.0204	3.92
362 AISI 94 B17 (Mod)	0.084	0.0838	1.19
363 Cr-V (Mod)	0.050	0.0499	1.00
364 High Carbon (Mod)	0.240	0.2406	0.21
High alloy steels			
344 Cr 15-Ni7-Mo2-A11	0.076	0.0756	1.06
348 Ni26-Cr15 (A286)	2.24	2.2405	0.02
Stainless steels			
121$_d$ Cr17-Ni11-Ti0.3 (AISI 321)	0.342	0.3420	0.12
Cast steel			
1146 White cast iron	0.20	0.2008	0.50
1173 Ni-Cr-Mo-V steel	0.015	0.0153	5.23
Aluminium-base alloys			
85b Wrought (chip)	0.022	0.0225	2.67
858 Alloy 6011	0.042	0.0421	0.95
859 Alloy 7075	0.041	0.0408	2.00
Copper "Benchmark"			
393 Unalloyed Cu"O"	0.5	0.5003	0.10
Special ingot irons and low alloy steels			
462 Low alloy B	0.058	0.0579	1.38
<u>Titanium ppm</u>			
Plain carbon steels			
11h BOH, 0.2C	1.92	1.92	0.52
874 Cupro-Nickel, 10% (CDA 706 High purity)	0.05	0.05	6.00
875 Cupro-Nickel, 10% (CDA 706) "Doped"	0.10	0.09	1.11

TABLE 15

Concentrations of titanium in industrial effluents, plants and soil

Sample	Titanium found, ppm[a]	
	Present method	AAS
Soil samples	10-200	8-190
Plants	4-390	4-390
Pulp and paper industrial effluents	45-145	40-130
Paint and pigment industrial effluents	100-200	100-200
Chrome industrial effluents	1-10 (mg/g)	1-10 (mg/g)
Monozite sand	5-25 (mg/g)	5-25 (mg/g)

[a] Average of eight determinations.

TABLE 16

Determination of traces of vanadium in high purity grade metals and alloys

Certified NBS Standard reference materials (SRM) samples

Sample	Certified value vanadium (%)	Vanadium, found		
		Spectrophotometry (%)	Co-efficient of variation (%)	AAS (%)
	Plain carbon steel			
124 BOH,0.4C	0.003	0.0029	17.24	0.0030
19_g AOH,0.2C	0.012	0.0119	3.36	0.0119
	Low alloy steels			
361 AISI 4340	0.011	0.0112	4.46	0.0109
363 Cr-V (Mod)	0.310	0.3098	0.19	0.3097
364 High carbon (Mod)	0.105	0.1051	0.38	0.1055
	High alloy steels			
344 Cr 15-Ni7-Mo2-AJI	0.040	0.0408	1.23	0.0405
348 Ni26-Cr 15 (A 286)	0.250	0.2498	0.32	0.2495
	Stainless steel			
1336 Cr 13-Mo03503	0.071	0.0712	0.98	0.0713
339 Cr 17-Ni9-Se02 (SAE 303 Se)	0.058	0.0579	1.38	0.0583
	Ingot iron and low alloy steels			
407_aD807_aCr-V	0.145	0.1449	0.21	0.1454
	Special ingot irons and low-alloy steels			
462 low alloy B	0.058	0.0582	0.86	0.0577
	Vanadium ppm			
Plain carbon steels				
152_a BOH, 0.5C	0.51	0.50	0.8	0.49

TABLE 17

Vanadium in the environment and rock samples

Sr. No.	Sample	No. of determinations	Vanadium found, ppm		Standard deviation
			AAS	Photometric present method	
1.	Onion	7	6.50	6.50	±0.01
2.	Carrots	7	3.52	3.50	±0.02
3.	Rice	9	1.00	0.98	±0.02
4.	Peas	9	0.75	0.70	±0.03
5.	Cabbage	9	6.02	6.00	±0.02
6.	Tobacco	9	2.25	2.20	±0.02
7.	Lake water	9	1.00	1.05	±0.03
8.	Sea water	9	0.80	0.80	±0.02
9.	Effluents I	5	1.20	1.20	±0.01
10.	Effluents II	9	0.07	0.05	±0.02
11.	Potato	5	5.75	5.75	±0.01
12.	Blood sample**	6	0.22	0.20	±0.02
13.	MS - I*	7	-	320	±0.2
14.	DV - I*	8	-	310	±0.1
15.	DV - III*	7	-	310	±0.1

* Samples from Mussoories phosphate deposites

** Whole blood samples from adult males

The data on the determination of titanium and vanadium are given in the Tables 14-17.

These data show that the present spectrophotometric method is very selective and sensitive for the trace determination of metals and can be easily used for the routine analysis. The comparison of the data obtained by atomic absorption spectrophotometry show the good agreement with those of present spectrophotometric method.

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