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INTRODUCTION

In this report is described, in a format suitable for inclusion in the I.W.D. Analytical Methods Manual, the methods developed for the analysis of environmental samples by ICAP.

These methods are:

1. Metals, by ICAP
2. Metals, preconcentration of water samples by chelation solvent extraction.
3. Metals, preconcentration of water samples by evaporation.
4. Metals, digestion and extraction of fish samples for determination of trace metals.
5. Metals - digestion of fish for ICAP analysis.

METALS (BY ICAP)

1. Scope and Application

1.1 This method can be applied to the determination of metals in all types of water samples and in fish.

1.2 The detection limits are dependent on the water sample type and the pre-concentration procedure used. They are listed in Table 1.

2. Principle and Theory

2.1 Atomic emission spectrometry using Inductively Coupled Argon Plasma excitation (ICAP) is based on the principle that when elements are exposed to the very high temperature of about 7000°K at the centre of the plasma, many of them will emit light of their characteristic wavelengths. Resolving this light in a spectrometer allows the simultaneous determination of many elements in the sample.

2.2 In this method the sample solution is sprayed into a chamber. A portion of this spray is dried and desolvated and the resulting aerosol is swept into the centre of the plasma. The flow through the system is shown in Figure 1.

2.3 To overcome any 'background' problems the 'zero' for each sample is obtained by making a measurement just off the analytical peak as the sample is aspirated. This is done by moving the primary slit of the spectrometer. The wavelength shift used is 0.023, 0.034 and 0.046 nm below the peak for measurements made in the third, second and first order respectively.

2.4 The ability to scan with the primary slit also gives the option to plot the profile of each analytical peak obtained from the sample and hence obtain further confirmation of the presence of the element.

3. Interferences

3.1 There are virtually no spectral interferences in this method.

3.2 There are some matrix effects because the physical properties of the aerosol formed in the spray drying process affects the amount of aerosol reaching the plasma. To overcome this the sample and standards are matrix matched when analyzing batches of similar samples. When single samples are analyzed a single standard addition is made to a replicate sample to obtain a calibration of the instrument.

4. Sampling Procedure and Storage

4.1 See Metals: General (Atomic Absorption).

5. Sample Preparation

5.1 See Metals: General (Atomic Absorption) for a discussion of the terminology and a list of the sample preparation options that are available.

5.2 This method describes the procedure for the analysis of a sample that has been treated and/or preconcentrated. For the procedures used in these processes see the appropriate section which may be one of:

Metals: preconcentration of water samples by evaporation.
Metals: preconcentration of water samples by chelation-solvent extraction.
Metals: digestion and extraction of fish samples for determination of trace metals.

6. Apparatus

6.1 Pump: Pump I (Technicon Corp.).

6.2 Sampler: Sampler IV (Technicon Corp.).

6.3 Nebulizer: concentric glass nebulizer (E. Meinhard Associates).

6.4 Spray chamber - shown in Figure 2.

6.5 Spray chamber heater shroud - shown in Figure 2.

6.6 Heater Lamp - 600 watt, 115 VAC quartz-halogen lamp (Cole Parmer - Cat. No. C3151-30).

6.7 Variable Transformer (applies 55V AC to lamp).

6.8 Desolvation condensers - shown in Figure 2.

6.9 ICP torch compartment and Model QA-137 spectrometer (Applied Research Laboratories). The grating has 1080 lines mm^{-1} and is blazed at 600 nm. Measurements are made in the first 3 orders. The wavelength and orders used are shown in Table 1.

6.10 Argon and helium gases are required to operate the ICAP equipment.

7. Reagents

7.1 Wash solution; 0.2% v/v HNO_3 in de-ionized water.

7.2 Stock metal solutions - see Metals: General (Atomic Absorption). The stock solutions required depend on the particular metals to be determined. The method is capable of simultaneously analyzing the following metals: Al, Cd, Co, CN, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, Ba, Sr, Cu, Mg, K, and Na.

8. Procedure

8.1 Set the ICAP system in operation with 0.2% HNO_3 wash solution. Turn on the heating lamp and cooling water and, when condition have stabilized, which takes about 30 minutes, start pumping samples and standards to the spray chamber.

8.2 Aspirate the sample for 2½ minutes, follow it with a 1 minute wash.

8.3 Integrate the signal from the sample for 50 seconds off-peak, then 50 seconds on-peak.

8.4 When samples that have a similar matrix are being analyzed, calibrate the instrument with a matrix-matched standard that contains the trace metals at a 1 mg L^{-1} level.

8.5 Calibrate the instrument for major ions, i.e. those metals that occur at levels above 1 mg L^{-1}, using the matrix-matched standards by the hitching-post technique.

8.6 When individual samples are being analyzed, if it is more convenient than the procedure above, calibrate the instrument by making a standard addition (at 1 mg L^{-1} for the trace metals) to a replicate sample.

9. Calculations

9.1 Calculations of concentrations are made in the computer part of the ICAP system.

10. Precision and Accuracy

10.1 Typical precisions that are obtained are shown in Table 2 where the results of the 5 replicate analyses in each of 5 Niagara River water samples are shown.

11. References

11.1 P.D. Goulden and D.H.J. Anthony, "Determination of Trace Metals in Fresh Waters by Inductively Coupled Argon Plasma Atomic Emission Spectrometry Using a Heated Spray Chamber and Desolvation." Analytical Chemistry, 54, 1678-82, (1982).

Table 1. Wavelengths, Orders and Detection Limits

Metal	Wavelength nm	Order	Detection Limits		
			Water-Preconcentration		Fish
			Evaporation $\mu g\ L^{-1}$	Solvent Ext. $\mu g\ L^{-1}$	$\mu g\ g^{-1}$
Al	308.22	2	3	-	-
Cd	226.50	3	0.05	0.01	0.01
Co	239.99	2	0.3	0.05	0.05
Cr	267.72	2	0.3	0.05	0.05
Cu	324.72	2	0.6	0.1	0.1
Fe	259.94	2	0.2	0.1	0.1
Mn	257.61	2	0.03	-	-
Mo	202.03	2	0.3	0.05	0.05
Ni	231.60	2	0.3	0.05	0.05
Pb	220.35	3	0.6	0.1	0.1
V	311.07	2	0.2	0.05	0.05
Zn	213.86	3	0.07	0.05	0.05
Ba	455.40	1	0.20		
Cu	317.93	2	0.40		
K	766.49	1	10		
Mg	279.08	2	1		
Na	589.00	1	5		
Sr	407.77	1	0.03		

Table II . Results of Five Replicate Analyses of Five Niagara River Samples

Sample	1		2		3		4		5	
Element	m_a	s_b	m	s	m	s	m	s	m	s
$\mu g\ L^{-1}$										
Al	76.500	0.360	72.500	1.100	62.100	1.300	81.400	1.200	71.000	3.600
Cd	0.062	0.014	0.052	0.011	0.082	0.017	0.080	0.018	0.089	0.019
Co	0.230	0.040	0.210	0.120	0.190	0.090	0.280	0.050	0.250	0.120
Cr	0.850	0.040	0.520	0.110	0.950	0.070	0.720	0.090	0.870	0.130
Cu	4.220	0.050	3.510	0.170	8.950	0.150	6.460	0.390	7.510	0.260
Fe	121.000	2.100	86.700	0.640	88.900	0.750	140.000	1.800	113.000	2.500
Mn	8.040	0.070	2.840	0.020	6.480	0.050	8.790	0.090	7.080	0.130
Mo	0.670	0.190	0.950	0.090	0.450	0.100	0.380	0.100	0.550	0.150
Ni	2.180	0.100	1.560	0.150	2.760	0.140	2.220	0.080	2.250	0.240
Pb	0.510	0.100	0.590	0.240	0.780	0.350	0.950	0.280	1.110	0.460
V	0.360	0.040	0.320	0.090	0.330	0.080	0.360	0.070	0.390	0.080
Zn	2.600	0.019	1.420	0.026	2.930	0.032	6.010	0.057	2.280	0.066
Ba	10.800	0.160	10.600	0.140	9.690	0.050	9.760	0.190	10.100	0.170
Sr	138.000	1.100	141.000	0.520	135.000	1.200	135.000	2.200	133.000	2.500
$mg\ L^{-1}$										
Ca	43.900	1.230	44.400	0.620	39.900	0.920	41.400	0.250	41.900	0.710
K	1.290	0.040	1.340	0.020	1.210	0.030	1.230	0.030	1.280	0.030
Mg	8.120	0.310	8.140	0.170	7.820	0.210	7.960	0.080	8.090	0.160
Na	10.700	0.170	10.900	0.100	9.970	0.130	9.950	0.160	9.880	0.170

a - mean of five replicates
b - standard deviation

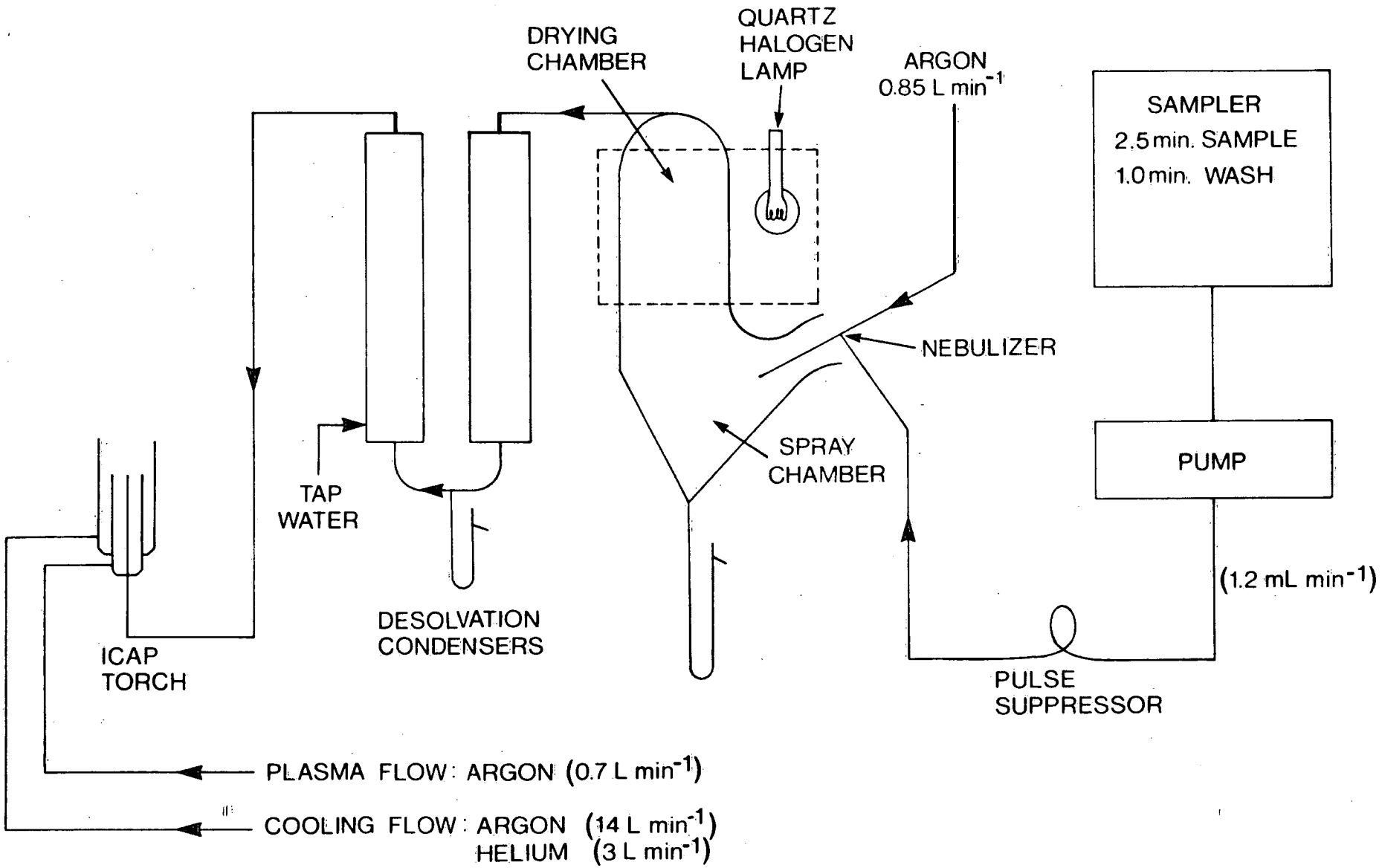
DRYING CHAMBER
QUARTZ HALOGEN LAMP
ARGON 0.85 L min-1
SAMPLER
2.5 min. SAMPLE
1.0 min. WASH
NEBULIZER
SPRAY CHAMBER
PUMP
TAP WATER
DESOLVATION CONDENSERS
(1.2 mL min-1)
ICAP TORCH
PULSE SUPPRESSOR
PLASMA FLOW: ARGON (0.7 L min-1)
COOLING FLOW: ARGON (14 L min-1)
HELIUM (3 L min-1)

Figure 1

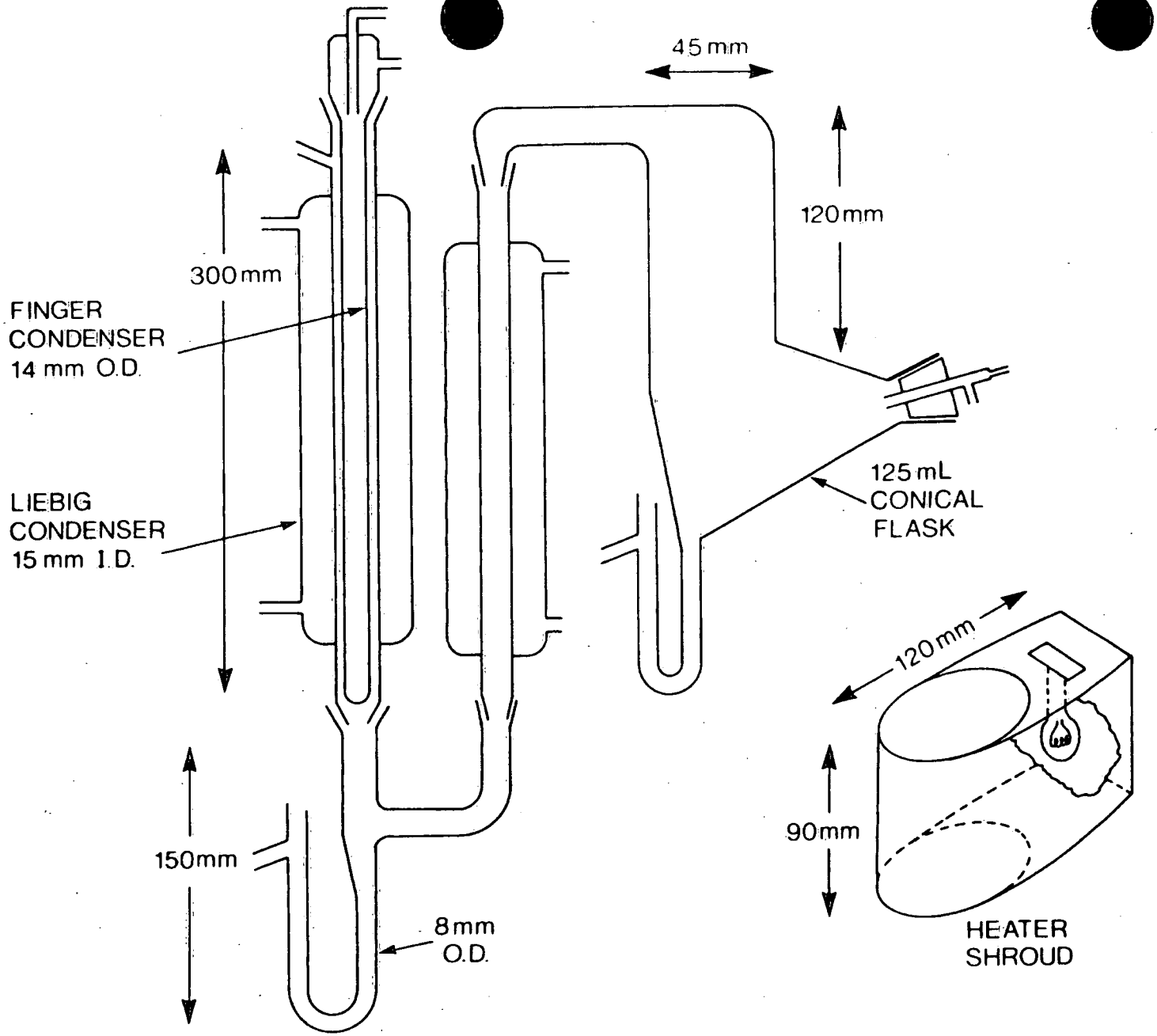
45 mm
120 mm
300 mm
FINGER
CONDENSER
14 mm O.D.
LIEBIG
CONDENSER
15 mm I.D.
125 mL
CONICAL
FLASK
120 mm
90 mm
150 mm
8 mm
O.D.
HEATER
SHROUD

Figure 2

M E T A L S

PRECONCENTRATION OF WATER SAMPLES BY CHELATION-SOLVENT EXTRACTION

1. Scope and Appliction

1.1 This method can be applied to the determination of metals in all types of water samples.

2. Principle and Theory

2.1 In this procedure, 10 trace metals are chelated with APDC (ammonium pyrrolidine dithiocarbamate) at pH 3.5 and extracted into chloroform. The chloroform is evaporated off and the extracted chelates are treated with nitric acid to destroy organic matter. The resulting aqueous solution is analyzed by ICAP.

3. Interferences

3.1 There are no interferences in this method.

4. Sampling Procedure and Storage

4.1 See Metals: General (Atomic Absorption).

5. Sample Preparation

5.1 See Metals: General (Atomic Absorption) for a discussion of the terminology and a list of the sample preparation options that are available.

6. Apparatus

6.1 Separatory funnels: 500 mL or 1 L funnels.

6.2 UV-grade silica tubes, 23 mm O.D., 170 mm long.

6.3 Aluminum hot block (this is the hot block used for digestions of fish).

7. Reagents

7.1 25% w/v ammonium acetate buffer, purify by extracting twice with 5 mL 1% APDC, 10 mL $CHCl_3$ per 100 mL solution and extract once with 10 mL $CHCl_3$ per 100 mL solution.

7.2 1% w/v APDC, purify by extraction with $CHCl_3$, 10 mL $CHCl_3$ per 100 mL solution.

7.3 4% w/v potassium persulfate solution.

7.4 Chloroform.

7.5 Nitric Acid (Ultrex - J.T. Baker).

8. Procedure

8.1 Take 400 mL water sample.

8.2 To 400 mL sample add 10 mL 4% $K_2S_2O_8$ (7.3) and boil for 60 minutes.

8.3 Cool sample and add ammonium acetate buffer (7.1) to bring sample pH to 3.5 (about 9 mL buffer is required).

8.4 Transfer sample to separatory funnel, add 20 mL chloroform and 20 mL APDC solution (7.2).

8.5 Shake funnel for 90 seconds, allow to stand for a few minutes to allow the layers to separate and collect the chloroform layer in a silica tube.

8.6 Add 10 mL $CHCl_3$ to separatory funnel and again extract. Add the chloroform extract to the silica tube above.

8.7 Add 2.0 mL nitric acid to the chloroform extract in the tube and evaporate most of the chloroform at room temperature with a stream of nitrogen gas.

8.8 Place tube in hot block and evaporate to near dryness.

8.9 Drive off remaining HNO_3 by evaporating three 1 mL portions of water. (After final evaporation, the tube should be dry).

8.10 Add 0.25 mL HNO_3 and 4.75 mL water to the tube.

METALS

PRECONCENTRATION OF WATER SAMPLES BY EVAPORATION

1. Scope and Application

1.1 This preconcentration procedure is applicable to all waters.

1.2 The procedure is described for a typical water from the Great Lakes, for which a concentration factor of 10 is used.

1.3 Depending on the total solids content of the water a greater or lesser concentration factor than the 10 above may be desirable.

2. Principle and Theory

2.1 The water sample is placed in a UV-grade silica tube and evaporated to small volume in a hot air oven.

2.2 The concentrated sample is digested with acid in a hot block and made up to small volume with water.

2.3 To avoid the need for sample transfers and hence minimize the possibility of contamination, the original and final sample quantities are determined by weighing the tube.

2.4 To prevent bumping in the concentration process, nitrogen gas is bubbled through the solution via a length of 'Teflon' spaghetti tubing.

2.5 UV-grade silica tubes are used for the concentration and digestion process to avoid the pick-up of metals, particularly aluminum, that may occur when borosilicate glass equipment is used.

3. Interferences

3.1 The interferences in the procedure arise only from the total solids content of the sample. If this is too high for the concentration factor used, there will be precipitation in the concentrated digest. This is avoided by selection of the appropriate concentration factor.

4. Sampling Procedure and Storage

4.1 See metals: General (Atomic Absorption).

5. Sample Preparation

5.1 See Metals: General (Atomic Absorption) for a discussion of the terminology and a list of the sample preparation options that are available.

6. Apparatus

6. Forced Air Oven.

6.2 UV-grade silica tubes - 23 mm O.D., 170 mm long.

6.3 Anti-bumping system - glass manifold connected to a nitrogen cylinder. To the manifold are attached numerous pieces of AWG30 'Teflon' tubing, each 350 mm long.

6.4 Aluminum hot-block (this is the same hot block system used for digestion of fish samples).

6.5 Top loading balance. (Mettler P1200 or equivalent).

7. Reagents

7.1 Nitric Acid (Ultrex, J.T. Baker Chemical Co.).

8. Procedure

8.1 Add 35 g of sample to a tube.

8.2 Place the tube in the rack in the oven and insert the Teflon tube into the sample.

8.3 Adjust the pressure on the Nitrogen Cylinder regulator so that about 1 mL min^{-1} gas is blown through the sample.

8.4 Turn the oven on and set the temperature controller for 180°C.

8.5 Evaporate the sample to about 2 mL volume.

8.6 Add 0.5 mL nitric acid and transfer the tube to the hot block.

8.7 Evaporate to near-dryness.

8.8 Add 1 mL water and evaporate to dryness.

8.9 Repeat 8.8 twice more.

8.10 Add 0.35 mL nitric acid and 1 mL water.

8.11 Add water to bring the weight of the sample to 3.5 g.

METALS

DIGESTION AND EXTRACTION OF FISH SAMPLES FOR DETERMINATION OF TRACE METALS

1. Scope and Application

1.1 This is a modification of the digestion procedure for fish that is currently used to determine Cu, Zn, Cr, Cd, Ni, and Pb. [Trace Metals in Fish; (Atomic Absorption)].

1.2 The digestion procedure is the same as that currently used up to the point where the clear solution of the fish in sulfuric acid is obtained.

1.3 The procedure described here can be used for the determination of Co, Fe, Mo, and V in addition to the six other metals.

2. Principle and Theory

2.1 The procedure differs from current procedure in that the sulfuric acid digest is neutralized with ammonia, the Cr is oxidized to Cr (VI) with bromine and the trace metals are extracted with APDC-chloroform. The extract is digested

with nitric acid and the resulting aqueous solution is analyzed by ICAP.

2.2 To avoid bumping in the heating processes, nitrogen gas is bubbled through the solutions via 'Teflon' tubing. This also serves to mix the solutions.

3. Interferences

3.1 There are no interferences in the method.

4. Apparatus

4.1 UV grade silica tubes, 3 mm O.D., 170 mm long.

4.2 Anti-bumping system, glass manifold connected to a nitrogen cylinder. To the manifold are attached numerous pieces of AWG 30 'Teflon' tubing, each 350 mm long.

4.3 Separatory funnels - 250 mL.

5. Reagents

5.1 Nitric Acid (Ultrex, J.T. Baker Chemical Co.).

5.2 Ammonium Hydroxide (Baker Instraanalyzed Reagent, J.T. Baker Chemical Co.).

5.3 Chloroform.

5.4 Bromine Water, 1% solution.

6. Procedure

6.1 When the sulfuric acid digest is clear, cool and add water to bring the volume to about 30 mL. This is after step 8.1.13 in "Trace Metals in Fish (Atomic Absorption).

6.2 Add 12 mL ammonium hydroxide (5.2).

6.3 Add 2 mL bromine water (5.4).

6.5 Heat in hot block until the colour from the bromine water has disappeared.

6.6 Cool, and transfer solution to the separatory funnel. Add 50 mL water.

6.7 Add 20 mL APDC solution and 20 mL chloroform.

6.8 Shake for 90 seconds. Allow to separate and put chloroform extract in a silica tube.

6.9 Add 2.0 mL nitric acid to the chloroform extract in the tube and evaporate most of the chloroform at room temperature with a stream of nitrogen gas.

6.10 Place tube in hot block and evaporate to near dryness.

6.11 Drive off remaining HNO_3 by evaporating three 1 mL portions of water. (After final evaporation, the tube should be dry).

6.12 Add 0.25 mL HNO_3 and 4.75 mL water to the tube.

METALS - DIGESTION OF FISH FOR ICAP ANALYSIS

1. SCOPE AND APPLICATION

1.1 This digestion procedure is applicable to any fish sample.

1.2 The procedure is used to determine Cd, Cu, Cr, Ni, Pb, and Zn.

1.3 Any other metals which may be of significance in a biological study can also be simultaneously determined, e.g. Co, Mn, Mo, V, Sr, Ba, etc.

2. PRINCIPLE AND THEORY

2.1 The fish sample is dissolved in nitric acid containing a small amount of sulfuric acid. The solution is evaporated and heated to the point where the residual fish tissue is charred and converted to carbon black. This is then dissolved in a HNO_3 - H_2O_2 mixture. The small amount of sulfuric acid serves to help char the tissue and also to act as a 'keeper' to prevent loss of metals by volatilization.

2.2 This procedure is used because there is a large loss of sensitivity if there is a significant amount of sulfuric acid in the solution used for ICAP analysis.

2.3 Glass shields are used around the culture tubes when the acid in the mixture is being evaporated. These reduce the heat loss from the tubes and help speed up the digestion procedure.

3. INTERFERENCES

3.1 There are no interferences in this procedure.

4. SAMPLING PROCEDURE AND STORAGE

4.1 The whole fish, or selected portions of the fish are ground in a meat grinder.

4.2 The resulting fish 'paste' is stored in a glass jar in a freezer.

5. SAMPLE PREPARATION

5.1 The fish 'paste' is weighed directly from the storage jar into the beaker used in the digestion procedure.

6. APPARATUS

6.1 Borosilicate culture tubes 18 x 150 mm.

6.2 Glass shields, glass tubing, 22 mm O.D., 95 mm long.

6.3 Beakers, 20 mL.

6.4 Hot Plate, Corning PC351 or equivalent.

6.5 Electric Hot Block, Tecam Driblock DB-3H or equivalent.

6.6 Anti-bumping manifold (see metals-preconcentration of Water Samples by Evaporation).

6.7 Glass Spatula.

7. REAGENTS

7.1 Nitric Acid

7.2 Sulfuric Acid

7.3 Hydrogen Peroxide

8. PROCEDURE

8.1 Weigh 1.2 to 1.5 g ground fish into a 20 mL beaker.

8.2 Add 0.1 mL H_2SO_4, 2 mL HNO_3.

8.3 Allow the initial reaction to subside, then warm to about 70°C on the hot plate.

8.4 Pour the contents of the beaker into a culture tube.

8.5 Add 2 mL HNO_3 to the beaker, warm the acid to about 70°C and use this to transfer the remainder of the fish sample to the culture tube.

8.6 Digest tube in the hot block at 120°C for 30 minutes.

8.7 Raise the temperature of the hot block to 180°C, place a glass shield around the tube.

8.8 Heat the tube for about 60 minutes, at this time the nitric acid will have boiled off and the contents of the tube will be black.

8.9 Cool tube, add 1 mL HNO_3, return to the hot block for 30 minutes.

8.10 Repeat 8.9.

8.11 Remove tube from block, allow to cool, add 1 mL H_2O_2, 1 mL HNO_3, return to block for 10 minutes.

8.12 Remove tube from block, allow to cool, add 1 mL H_2O_2, return to block for 5 minutes. At this stage the contents of the tube should be a clear liquid, light yellow in colour. If the solution is not clear or is dark coloured, repeat 8.12.

8.13 Make up the volume of the solution to 6 mL.

8.14 Prepare blank solutions by evaporating 7 mL HNO_3, 0.1 mL H_2SO_4, 2 mL H_2O_2 (3 mL H_2O_2 if 3 mL used above) in tubes. It is necessary to use the anti-bumping manifold when evaporating the blank solutions.

8.15 The samples and blanks are then determined via ICAP, using the off-peak measurement for the zero, the on-peak measurement for the sample value and a standard addition to determine the slope of the calibration line.

9. CALCULATION

9.1 From the concentration in the sample (C $\mu g\ L^{-1}$) and the blank value (b $\mu g\ L^{-1}$) the concentration in the fish (in $\mu g\ g^{-1}$) is calculated as follows:

$$\text{Metal in fish} = \frac{(c-b) \times 6}{\text{sample weight} \times 10^{3}}$$

(sample weight is in g)

10. PRECISION AND ACCURACY

10.1 Typical precisions obtained with the blank readings and with fish samples are shown in Table 1.

Table I. RESULTS OF BLANK AND FISH DETERMINATIONS (ug g^{-1} FISH)

Metal	Blank		Fish #1	
	Mean*	S.D.*	Mean*	S.D.*
Cd	0.0013	0.0009	0.083	0.011
Cr	0.096	0.010	0.30	0.042
Cu	0.095	0.026	1.25	0.29
Ni	0.024	0.012	0.18	0.026
Pb	0.038	0.023	0.82	0.027
Zn	0.093	0.090	9.8	0.75

* Means and Standard Deviations based on six replicates

15784