ISOTOPE DILUTION ANALYSIS OF ENVIRONMENTAL SAMPLES

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Abstract

Isotope dilution analysis has been used for the determination of several trace elements /especially metals/ in a variety of environmental samples, including aerosols, water, soils, biological materials and geological materials. Variations of the basic concept include classical IDA, substoichiometric IDA, and more recently, sub-superequivalence IDA. Each variation has its advantages and limitations. A periodic chart has been used to identify those elements which have been measured in environmental samples using one or more of these methods.

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For many years, various nuclear analytical techniques have been used in science and engineering, and more recently, for the analysis of environmental samples of diverse origin. These techniques include a broad range of approaches, including activation and non-activation procedures. Perhaps the single most important non-activation approach is isotope dilution analysis, IDA, which is based on the simple concept of conservation of an amount of radioactivity.

Isotope dilution analysis, and its many variants, has been used for the determination of trace elements /especially metals/ in a wide variety of environmental samples, including aerosols, water, soils, biological materials and so on.

The method can be useful in the following general situations:

- A substance is to be determined in a mixture of similar materials, but a quantitative isolation is impossible.
- The analyte occurs at a low concentration, so that losses such as sorption onto vessel surfaces, etc., during the separation procedures are inevitable.
- The analysis must be performed quickly, eg. because of decay or shifts in equilibria.
- The analyte is part of a large system, and only a part of it is available, eg. water in a large living animal.

CLASSICAL ISOTOPE DILUTION ANALYSIS

The classical technique uses the comparison of the specific activity of a radioactive tracer before and after mixing with a

non-radioactive compound which is to be determined /the analyte/. In other words, the radioactive tracer is "diluted" with its non-radioactive counterpart in the sample. The dilution causes a change in the specific activity of the added tracer, which can be measured and used to calculate the amount or concentration of the component of interest in the sample. The basic concept is described in Flow Sheet 1, which includes the related mathematical equations.

Flow 1 Sheet

It should be noted that the condition $E_s = E_x$ refers to equal counting efficiency of samples and standards; and is crucial for reliable results. The term R_x/M_x should be independent of mass, and therefore can be measured on any pure portion of the compound separated from the sample, assuming that the sample is homogeneous, and that sufficient material is isolated for the reliable measurement of R_x and M_x. It should be noted that with this technique, it is not necessary to separate the analyte quantitatively from the sample, provided that the final counting sample is pure.

A number of variations of classical IDA have been developed, including:

- Direct IDA, or Single IDA, where the non-radioactive sample is diluted with a radioactive tracer,
- Reverse IDA, where a radioactive substance is diluted with a stable one,
- Derivative IDA, where the analyte is originally non-radioactive, but is made radioactive by a stoichiometric reaction with a radioactive reagent,

- Double isotope dilution, where two radioactive isotopes of the same element are used,
- IDA after activation, where the radioactivity of the analyte is induced by an appropriate activation technique,
- Pseudo IDA, in which the diluting analyte is not the same element as the tracer, but has adequately similar chemical properties.

The advantage of classical IDA includes:

- wide range of applicability. The method has been used for several elements, and many types of samples,
- in favorable cases, high sensitivity and precision,
- separation steps need not be quantitative.

Disadvantages of the method are:

- suitably labeled compounds may be unavailable or expensive,
- the tracer must be equilibrated with the sample; there must be complete isotopic exchange,
- the compound isolated for counting and determination of amount /eg. by weighing/ must be chemically pure,
- enough compound must be isolated so that a suitable measurement of amount of material /eg. mass/ can be made.

Perhaps the main disadvantage of the classical method is the necessity of a second type of measurement, so that specific activities can be determined. This limits the sensitivity of the method.

It is beyond the scope of this paper to give a comprehensive survey of all the applications of classical IDA in environmental studies. Table 1 presents a concise summary,

Table 1

and it serves to illustrate the broad range of elements and sample types that have been studied. It includes at least thirteen elements, and sample matrices such as water, soil, plants and animals. Separation procedures include precipitation, distillation, solvent extraction, coprecipitation, etc. Methods used for yield /mass/ determinations include gravimetry, colorimetry, fluorometry, flame photometry, etc.

SUBSTOICHIOMETRIC IDA

As pointed out above, the principle handicap of classical IDA is the need for measurement of the amount of pure substance isolated so that specific activities can be determined. This requirement limits the sensitivity of the method, which is important in the analysis of environmental samples.

However, in the basic equation, only the ratio of specific activities occurs. This means that if exactly the same amount /or an exact multiple/ of material can be isolated from sample and standard, the equations simplify drastically. This concept is the basis of a very important branch of IDA, namely substoichiometric IDA, which is outlined in Flow Sheet 2.

Flow 2 Sheet

Thus, in principle at least, it is only necessary to isolate exactly equal /or exact multiples/ of a desired compound from both sample and standards. The analyst can fix the amount isolated by adding a controlled, substoichiometric amount of suitable reagent to sample and standard prior to any separation steps. /Hence the name "Substoichiometric IDA"./ The exact amount of reagent consumed, and the exact ratio by which the analyte reacts with it need not be known, only a constant ratio is necessary. Of course, the reaction

product must be separable from the sample and standard, and it must be suitable for counting.

Another important advantage of substoichiometric IDA is enhanced selectivity due to competition for the separation reagent between the analyte and any interfering substances. In favorable cases, this competition will minimize the transfer of interferences into the final counting samples. Selectivity can be further enhanced by using masking agents to decrease the effective concentration of the interferences, or by using a pre-concentration step.

It is clear that the selection of a suitable separation reagent is a critical step in the development of a substoichiometric method. Some criteria include:

- sufficiently large stability constants for any complexes or other separable compounds formed, and significant differences among these constants for different elements /selectivity/,
- stability /thermal, photochemical, etc./ in solutions at extremely low concentrations,
- formation of only one type of complex /or compound/ with the analyte under a given set of conditions,
- favorable kinetics of complex /or compound/ formation, and of separation,
- no sorption on reaction container surfaces.

Some of the methods used for isolating equal amounts of material from sample and standard are:

- extraction of complexes
- electrolysis
- sorption
- ion exchange reactions
- precipitation

There has been a considerable effort to expand the scope of substoichiometric IDA, and several variations have been proposed:

- Direct Substoichiometric IDA, with the addition of a labelled element, or with induced radioactivity,
- Reversed Substoichiometric IDA, including activation analysis with substoichiometric separation and determination of the concentration of naturally occuring radioactive elements,
- Displacement Substoichiometry, in which the basic reaction is not the formation of a stable complex with the analyte, but the partial decomposition of a complex by fractional displacement with a second substance which has a larger stability constant,
- Redox Substoichiometry, in which partial oxidation or reduction of the analyte is followed by the transfer of the reacted /or unreacted/ portion to a second phase.

The sensitivity of substoichiometric IDA is usually limited by one of the following factors:

- specific activity of the tracer,
- chemical stability of the separation reagent and separation product,
- kinetic factors,
- values of any blanks, and background count rates.

Substoichiometric IDA techniques have been developed for an impressive list of elements in environmental samples. A partial, but illustrative, list of applications is given in Table 2. Seventeen elements are included, measured in

Table 2

samples as diverse as biological materials, rocks and ores, freshwater, sediments, blood, teeth, seawater, etc.

SUB-SUPEREQUIVALENCE IDA

The basic requirement of substoichiometric IDA poses a stringent constraint, namely, that equal amounts of material must be isolated from sample and standard. This can be difficult, if not impossible, for a series of samples of widely varying composition or concentration. Ideally, sample and standard would have the same composition.

The sub-superequivalence methods were developed in order to minimize this constraint. The basic method involves the procedure as outlined in Flow Sheet 3 [35,36].

Flow 3 Sheet

The solution to be analyzed is labelled with an appropriate isotope, and two series of aliquots are taken. In the first series /Series 1/ each aliquot contains the same amount of analyte /x/ and activity /A_o/. In the second series /Series 2/, each aliquot contains a K times greater amount of material and activity than the first /Kx and KA_o/. The first series is isotopically diluted by adding incremental amounts of the non-radioactive form of the analyte /$y_j = y_1, y_2 \ldots$/. This gives a series of isotopically diluted aliquots /$x+y_1$, $x+y_2 \ldots$/. If all aliquots of both series are now brought to the same volume, the concentration of one in Series 1 will be equal to that of Series 2:

$$\frac{x+y_k}{V} = \frac{Kx}{V} \quad .$$

If to all aliquots we add the same amount of a reagent which will react with the analyte, the amount of the product generally will depend on the concentration of the aliquot. Furthermore, solutions of the same concentration would form the same amount of product. This fact makes analysis possible, provided that a reproducible separation and counting procedure can be found.

The same amount of product is isolated from each of the non-diluted aliquots /M_2 is a constant in Series 2/ with the same activity /A_2/. The aliquots of Series 1 will yield varying amounts of product /M_{1j} = M_1, M_2 .../ and varying activities /A_{1j} = A_{11}, A_{12} .../.

In dilution with non-radioactive material, the amount of radioactive material remains constant; hence we may write the set of equations as given in Flow Sheet 3.

In other words, the amount of unknown in a given volume of sample /x/ can be determined from the intersection of I = K with $y = y_k$. Note that it is not necessary to measure M_{1j} or M_2, which are the amounts of material isolated from Series 1 and 2.

Four variations of the basic method have been proposed, based on increasing the amount of radioactive tracer instead of inactive material, and dilution with the radioactive tracer instead of with the non-radioactive one.

The main advantages of the sub-superequivalence method include:

- higher sensitivity in systems where stability constants limit the sensitivity of substoichiometric IDA,

- systems can be studied where changing complex composition makes isolation of equal amounts of material impossible,
- only one phase need be measured.

Sub-superequivalence methods have been used in a growing number of instances for the analysis of environmental samples. Table 3 gives a summary of examples. At least eleven metals have been determined, mainly in water samples.

Table 3

CONCLUSION

It is apparent from what has been said that IDA has become a valuable method for the analysis of environmental samples. Figure 1. is a periodic chart, showing those elements which have been determined in environmental samples /26/; those which have been measured by classical IDA /55/; elements measured by substoichiometric IDA /40/; and those which have been measured by sub-superequivalence IDA /12/.

Fig.1

While it is indeed clear that IDA can be very useful for the environmental scientist, much work needs to be done in the area of verification and optimization of these techniques before they can be widely accepted for routine environmental samples.

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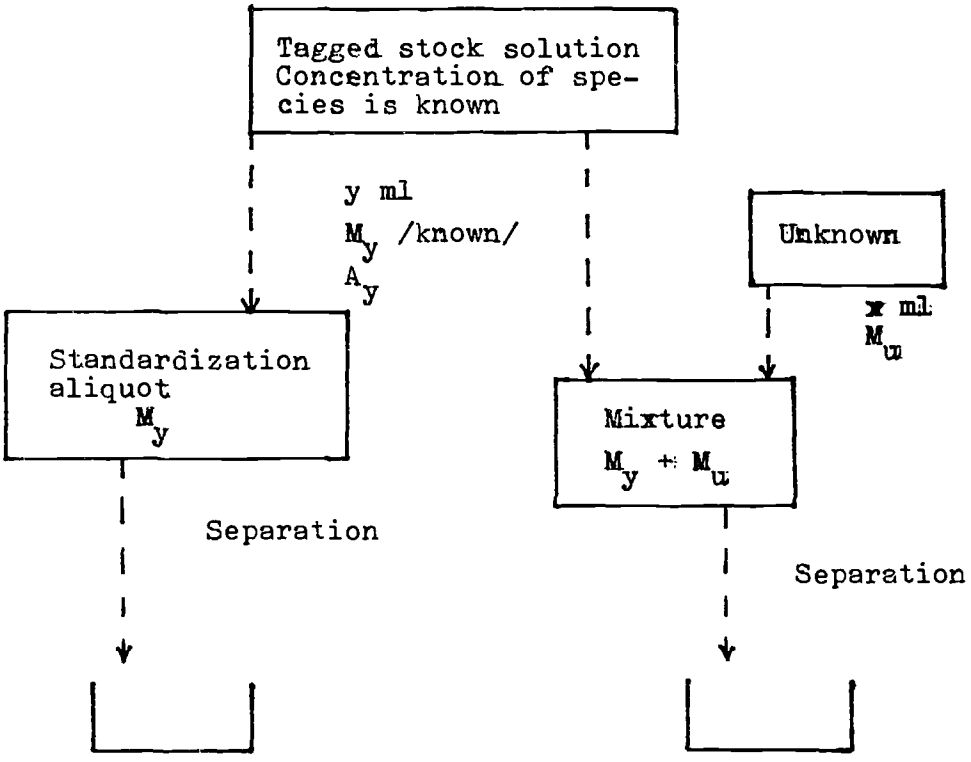
Flow Sheet 1. Classical Isotope Dilution Analysis



Counting sample

$$R_s,\ M_s,\ S_s = \frac{R_s/E_s}{M_s} = A_s/M_s$$

R: Cpm
M: Mass
E: Detection efficiency
A: Activity
S: Specific activity = A/M
V: Volume
C: Concentration

Counting sample

$$R_x,\ S_x = \frac{R_x/E_x}{M_x} = A_x/M_x$$

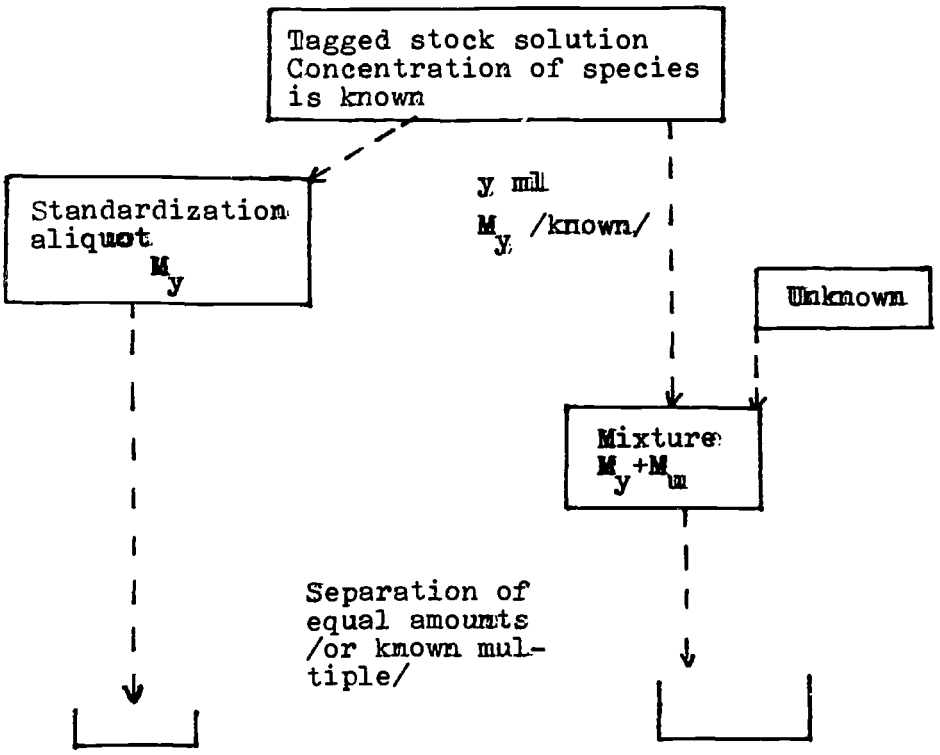
$$A_y = S_y M_y = S_x(M_y + M_u) = S_x M_x + S_x M_u$$

$$M_u = M_y\left(\frac{S_y}{S_x} - 1\right) = M_y\left(\frac{R_s/E_s M_s}{R_x/E_x M_x} - 1\right)$$

If $E_x = E_s$, then:

$$M_u = M_y\left(\frac{R_s/M_s}{R_x/M_x} - 1\right)$$

Flow Sheet 2. Basic Substoichiometric IDA



$$S_s = \frac{R_s/E_s}{M_s} = A_s/M_s \qquad S_x = \frac{R_x/E_x}{M_x} = A_x/M_x$$

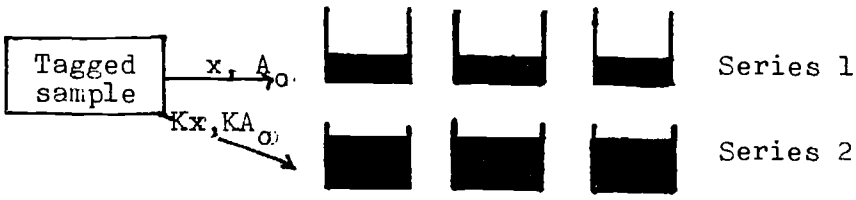
$M_s = M_x$ or $M_s = a\,M_x$: Equal amounts, or exact multiple

$$M_u = M_y \left(\frac{R_s/M_s}{R_x/M_x} - 1 \right)$$

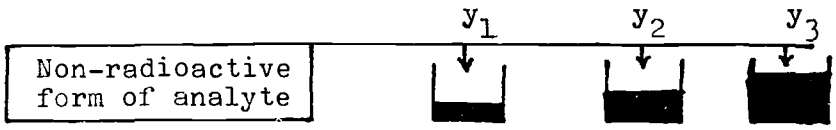
$$M_u = \left(\frac{R_s}{R_x} - 1 \right) \quad \text{or} \quad M_u = \left(\frac{a\,R_s}{R_x} - 1 \right)$$

Flow Sheet 3. Sub-superequivalence IDA

Step 1. Preparation of two series of aliquots from tagged sample.



Step 2. Addition of incremental amount of non-radioactive form of analyte to Series 1.



Step 3. Adjustment of all aliquots to same volume. There will be one aliquot in Series 1 for which we may write:

$$(x + y_k)/V = Kx/V$$

Step 4. Addition of same amount of separation reagent /SR/ to all aliquots. Formation of separation product.

Step 5. Separation and counting of separation product.

Conservation of activity: $(x+y_j)(A_{1j}/M_{1j}) = (Kx/K)(A_2/M_2) = xA_2/M_2$

$$I_j \equiv A_2/A_{1j} = \frac{M_2}{M_{1j}}\left(\frac{x+y_j}{x}\right) = \frac{M_2}{M_{1j}}\left(1 + y_j/x\right)$$

$I_K = K$; $M_{1K} = M_2$; $y_j = y_k$

$K = 1 + y_k/x = (x+y_k)/x$

$y_k = x(K-1)$

$x = y_k/(k-1)$

The unknown amount of material, x, can be calculated from the intersection of I_K and y_k.

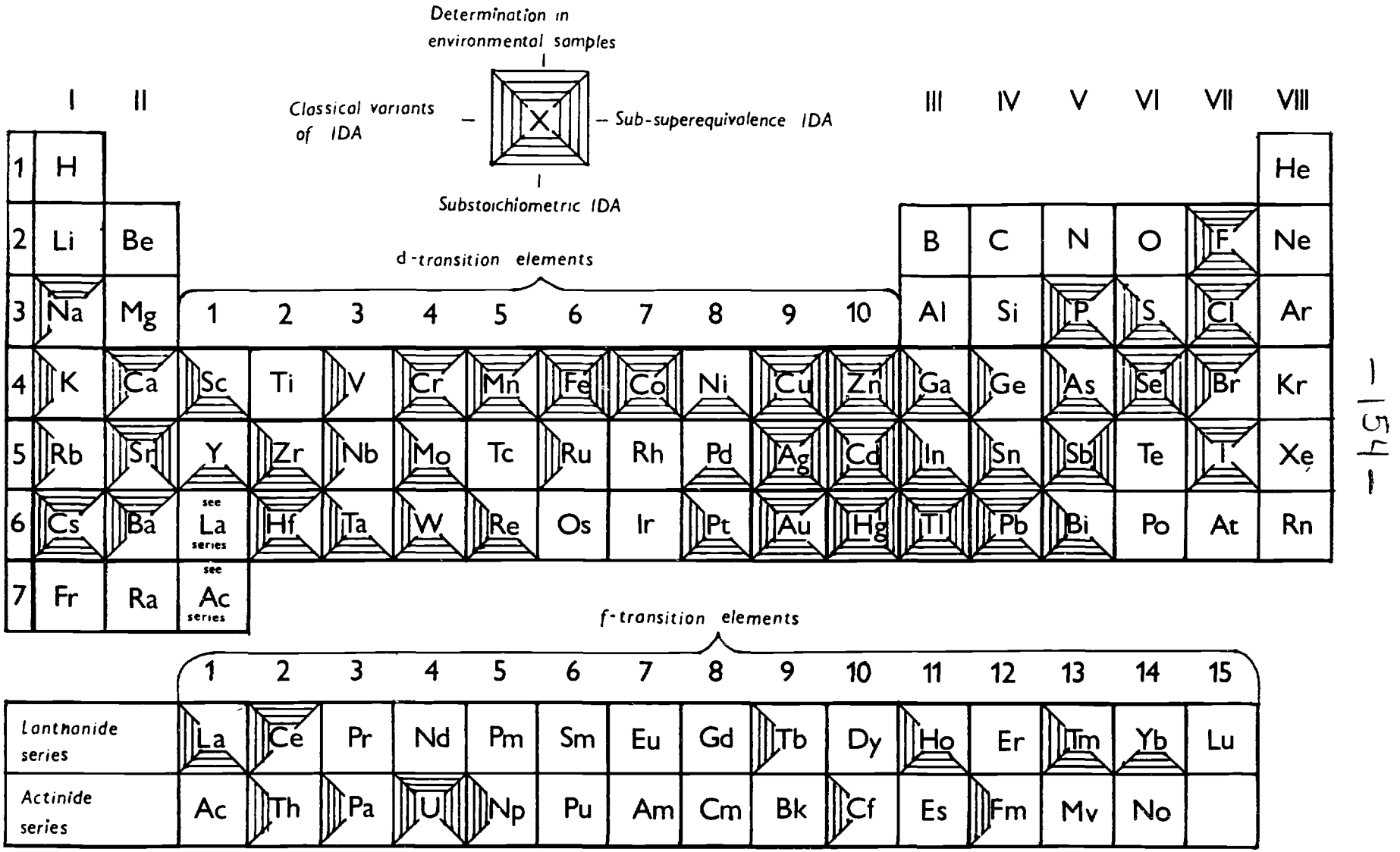

Determination in environmental samples
Classical variants of IDA
X
Sub-superequivalence IDA
Substoichiometric IDA
I
II
III
IV
V
VI
VII
VIII
d-transition elements
1 2 3 4 5 6 7 8 9 10
f-transition elements
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
1 H
2 Li Be
3 Na Mg
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
6 Cs Ba see La series Hf Ta W Re Os Ir Pt Au Hg
7 Fr Ra see Ac series
B C N O F
Al Si P S Cl
Ga Ge As Se Br
In Sn Sb Te I
Tl Pb Bi Po At
He Ne Ar Kr Xe Rn
Lanthanide series La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinide series Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Mv No

Table 1.

Determination of Trace Elements in Environmental Samples by Classical IDA [1]

Element determined	Matrix	Tracer	Separation process	Mass determination	Amount determined
Ba	Binding materials	^{140}Ba	Sediment		0.23-1.3 mg
	Biological material	^{140}Ba	Precipt.	Gravimet.	
Ca	Binding materials	^{45}Ca	Sediment.		1.2 mg
	Soils /exchangeable Ca/	^{45}Ca			
	Water Hardness	^{45}Ca	Precipt.	Gravimet.	
Ce	Vegetables	^{130}Ce	Precipt.	Gravimet.	
Cl	Biolog.fluids and tissues	^{36}Cl	Distillat.	Amp.titr.	20-40 meq
	Human body	^{82}Br	Precipt.		
Co	Biological materials, Vitamin B_{12}	^{60}Co	Solv.extr.	Spectrophotomet.	4-150 µg
Cr	Marine organisms	^{51}Cr	Solv.extr. precipt.	Colorimetry	1.0-5.0 µg
Cs	Sea water	^{137}Cs	Coprecipt.		
I	Biological material	^{131}I	Distillat.	Colorimetry	10 µg
Na	Exchangeable Na in human body	^{24}Na			
P	Soil	^{32}P	Precipit.	Gravimet.	
Se	Plant material	^{75}Se	Solv.extr.	Fluorometry	0-2-6.6 ppm
Sr	Binding materials	^{89}Sr	Sediment.		mg
	Sea water	^{85}Sr	Coprecipt.		
	Sea water	^{88}Sr	Coprecipt.	Flam.photometry	9-50 ppm
	Soil	^{90}Sr	Precipt.	Gravimet.	
Tl	Chamber dusts	^{204}Tl	Solv.extr.	Colorimetry	30-300 µg
U	Sea water	^{237}U	Cocrystall.	Fluorometry	
	Sea water	^{237}U	Solv.extr.	Fluorometry	3.0 µg

Table 2.

Determination of Trace Elements in Environmental Samples by Substoichiometric IDA

Element	Matrix	Tracer	Separation process	Reagent	Amount determined	Reference
Ag	Plant materials	^{110m}Ag	Solv.extr.	dithizone	0.15-0.9ppm	[2]
Au	Rock, ores	^{198}Au	Solv.extr.	dioctyl sulfide	$2.6x10^{-6}$%	[3]
	Rocks	^{198}Au	Solv.extr.	N-diethyldithiophosphate in CCl_4	$n.10^{-7}$%	[4]
Br, Cl	Meteorites, basalts	^{82}Br, ^{36}Cl	Precipt., Dialysis, Electrodial.	$AgNO_3$	10^{-5}- 10^{-6}g	[5]
Cd	Biolog.materials	^{109}Cd	Solv.extr.	dithizone	0.16-0.88 $\mu g.g^{-1}$	[6,7]
Cu	Blood	^{64}Cu	Solv.extr.	NaDDC	$n.10^{-3}$%	[8]
F	Teeth /enamel/	^{18}F	Adsorption	glass as sorbent	100 ppm	[10]
	Fluorinated,non-fluorinated water, urine	^{18}F	Solv.extr.	$/CH_3/_3SiCl$ in benzene	0.46-1.03 $\mu g.ml^{-1}$	[11]
		^{18}F	Solv.extr.			
	Plant materials	^{18}F	Solv.extr.	$/CH_3/_3SiCl$ in benzene	0.05µg	[12]
Fe	Biolog.materials	^{59}Fe	Solv.extr.	8-quinolinol	550 ppm	[13]
	Rock	^{59}Fe	Ion-exchange	8-quinolinol EDTA-cation resin column	1.9-9.32%	[31]
Hg	Biolog.materials	^{203}Hg	Solv.extr.	dithizone	50 70 µg	[14]
	Mineral water	^{203}Hg	Solv.extr.	dithizone	ppm	[15]
	Plants /rice/	^{203}Hg	Solv.extr.	dithizone	ppm	[16]
I	Environmental samples	^{131}I	Dialysis	$AgNO_3$	10^{-5}- 10^{-7}g	[17]
Mn	Biolog.materials	^{54}Mn	Synergistic extraction	TTA + 1,10-phenanthroline	68-235 $\mu g.g^{-1}$	[18]
Pb	Granites,	ThB	Solv.extr.	dithizone	28-40ppm	[19]
	Rock		Solv.extr.	EDTA-dithizone	7.3-56.2 $\mu g.g^{-1}$	[32]

Table 2. /Cont./

Element	Matrix	Tracer	Separation process	Reagent	Amount determined	Reference
SO_4^{2-}	Atmosph. precipitates	^{35}S	Precipit.	$BaSO_4$/EDTA	40ng.ml^{-1}	[20,21]
Sr	Biolog.materials	^{90}Sr	Solv.extr.	8-quinolinol	50-70 µg	[22]
Tl	Minerals,sediments, hydrothermal waters	^{202}Tl	Solv.extr., substoich. displacement	thallium/I/ dithizonate in CCl_4	42 ppm-0.88%	[23]
Zn	Sea water	^{65}Zn	Solv.extr.	dithizone	68 µg.l^{-1}	[24]
	River water	^{65}Zn	Ion-exchange	8-quinolinol-5-sulphonic acid, Anion resin column	0.12ppm	[33]
U	Granites	^{233}U	Solv.extr. with TTA in $CHCl_3$	Arsenazo III	1-40 ng	[25]

Table 3.

Determination of Trace Elements in Environmental Samples
by Sub-superequivalence IDA

Element	Matrix	Tracer	Separation process	Reagent	Amount determined	Reference
Ag	Water	^{110m}Ag	Solv.extr.	dithizone		[26]
Cd	Water	^{109}Cd	Solv.extr.	dithizone	$0.9 \mu g.ml^{-1}$	[34]
Cu	Water	^{64}Cu	Solv.extr.	dithizone		[26]
	Fresh water	^{64}Cu	Solv.extr.	thioxine	10^{-6}-10^{-7}g	[9]
Co	Vitamin B_{12} solution	^{60}Co	Ion-exchange	EDTA	$0.81 \mu g.ml^{-1}$	[27]
Fe	Water	^{59}Fe	Solv.extract.	cupferron		[26]
	Water	^{59}Fe	Solv.extr.	EDTA-acethyl-acetone	0.03 $\mu g.ml^{-1}$	[28]
Hg	Water	^{203}Hg	Solv.extr.	dithizone		[26]
Se	Water	^{75}Se	Solv.extr.	NaDDC-CCl_4	$1.92 \mu g.ml^{-1}$	[29]
Sr	Water	^{89}Sr	Solv.extr.	DC-18-crown 6	$1.12 \mu g.ml^{-1}$	[34]
Tl	Tl solution	^{204}Tl	Solv.extr.	Brillant Green-benzene	0.5-105 µg	[30]
U	Environmental samples	^{233}U	Solv.extr.	TTA		[26]
Zn	Fresh and sea water	^{65}Zn	Solv.extr.	thioxine	10^{-6} - 10^{-7} g	[9]