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GENERAL ASPECTS OF TRACE ANALYTICAL
METHODS — V

COMPARISON OF THE ABILITIES OF
TRACE ANALYTICAL METHODS TO
DETERMINE SMALL AMOUNTS OR
CONCENTRATIONS OF ELEMENTS

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Abstract. The report compares realistic "limits of determination" defined as $10 |s_{b1}|$, where $|s_{b1}|$ is the standard deviation of the blank, for most elements determined by the more common analytical techniques. Whilst recognising the necessarily approximate and transient nature of the data, it is believed that it will provide a valuable comparison of the capabilities of the techniques considered at the present time.

For many years representatives of the Analytical and Applied Chemistry Divisions have discussed the idea of collecting and tabulating data concerning effectiveness of the most important trace analytical methods for the determination of small amounts or concentrations of elements. In compiling this report the Commission on Microchemical Techniques and Trace Analysis recognizes the reservations which have always to be expressed if various analytical methods, many of them in a state of rapid development, are to be compared in this way. Therefore, this project can only be an attempt to give a temporary and approximate representation.

The ability of analytical methods to detect small amounts or concentrations is best expressed by the statistical term "limit of detection", which Kaiser (Ref.1) has defined as:

$$\bar{x} = \bar{x}_{b1} + k \cdot |s_{b1}| \quad \text{with} \quad c = f(\bar{x})$$

In these equations, which are accepted by IUPAC (Ref. 1a), \bar{x} is the smallest acceptable measureable signal and c the lowest concentration which can be measured by the analytical procedure, and k is a constant. To calculate \bar{x} the standard deviation s_{b1} and the mean value \bar{x}_{b1} of the blank are determined from at least 20 blank analyses. For this, all steps of the complex analytical procedure with their own contributions to the blank must be taken into account, including all reagents and vessels needed, all manipulations, and the electronic noise of the equipment. The factor k depends on the desired or required confidence; by convention $k = 3$ is mostly used, while $k = 6$ defines the guarantee of purity according to Kaiser (Ref.1).

Values of \bar{x} or c for a given analytical method are only valid in connection with the complete working instruction; each variation of one of the steps of an analytical procedure will lead to some change in the values of \bar{x} and c . Nevertheless, an examination of the literature shows that tabulated \bar{x} -values often are calculated from analytical results which have been obtained using highly optimized working conditions or even from idealized model analyses; frequently the value of the factor k is not given.

Additionally, there is often a lack of consideration of the numerous possibilities for systematic errors whose sources and magnitude also change with changes in sample material and analytical conditions. So tables of original data taken from publications, each of which describes the application of a special analytical method to a special analytical problem are mostly of little practical use.

Detection limit data for a method, without information about the sample, its pretreatment and all the details of the analytical procedure, at best can give only a very rough impression of the ability of the method to detect some selected elements or compounds. In consideration of this viewpoint, some simplifying assumptions seemed to be necessary in the present report with regard to a useful comparison and even to a reasonable evaluation of such data for various analytical methods.

1. Instead of the above "limit of detection":

$$\bar{x} = \bar{x}_{b1} + k \cdot |s_{b1}| \quad (k = 3)$$

a "limit of determination" L_Q was defined using $k = 10$ in the above formula (Ref. 1b,2). It was used to compile the capabilities of analytical methods in the following tables. These data are normally based only on the second part of the above equation: $10 \cdot |s_{b1}|$ under the following provisions (see items 2 and 3); exceptions are the data for spectrophotometric methods and for atomic absorption spectrometry whose calculation bases are explained below. In contrast to the factors $k = 3$ or $k = 6$ which are well defined from theoretical aspects, the factor $k = 10$ may be a more practical one, which allows a better consideration of the

uncertainty when the abilities of analytical methods in extreme trace analysis are compared. We also have to remember that the factor $k = 10$, like the factors $k = 3$ or $k = 6$, is based on a "normal Gaussian distribution" in spite of the fact that the results in trace analysis approach zero, which means that "non-Gaussian distribution" will frequently prevail. To overcome the problem of inhomogeneous dimensions of literature data which are presented in absolute quantities (g-scale) or concentrations (g ml^{-1} scale) the same symbol L_Q will be used in both cases. Therefore, this compilation should be only considered as a first attempt which needs a lot of further discussions and efforts to find a more satisfying solution.

2. The compiled data refer to the determination of elements in pure aqueous solutions which contain only the element in question. They are obtained by averaging literature data. Any combination of the methods of determination dealt with in this survey with special pretreatment techniques such as decomposition or preconcentration, as well as with micro techniques, are omitted. The only exception as regards the combination of preconcentration and determination is anodic and cathodic stripping voltammetry on account of its character, as mentioned at the end of the report.

3. The report is restricted to some of the most important analytical methods of general applicability used in trace analysis. The compiled data were obtained by the use of commercially available instruments and recommended analytical procedures from the literature. Because of this simplification of the procedure of data compilation, any application of the data as standard values in practical trace analysis must be subject to some restrictions. The data are a measure of the effectiveness of analytical methods with regard to the determination of amounts or concentrations of elements that are as small as possible. However, in trace analysis generalization from one analytical problem to another is not allowed because each different sample material may result in a completely new analytical situation leading to very different statistical and systematic errors, and changing the detection limit. Similarly considerable flexibility exists in the operational conditions under which many of the analytical techniques can be applied. Although literature data have been critically evaluated based on the present state of knowledge, the tabulated values can only represent approximations of the "true" limits of determination which are valid for each special analytical problem. Depending on the conditions the possibility of a variation of L_Q -values ($10 \cdot s_b$) over a range of one order of magnitude or more must be taken into account. Any generalization should be treated with caution. Nevertheless, the data compiled in this report may be usefully used as an initial survey of the effectiveness of different analytical methods regarding the determination of small quantities of elements. Moreover, critically applied, they may be helpful in selecting the most sensitive method for solving a non-routine trace analytical problem. The limits of determination for a wide range of elements and techniques are compiled below in connection with the following considerations.

1. Molecular absorption spectrometry (Table 1)

The values correspond to an absorbance of 0.025 for an absorption path length of 1 cm and an assumed absorbance error of ± 0.0025 assuming a sample consumption of 1 ml.

2. Atomic absorption spectrometry (AAS)(Table 1)

(a) Flame AAS. The values correspond to an absorbance of 0.005 and assume an absorbance error of ± 0.0005 , using conventional burners with a 10 cm-absorption path length and a sample consumption of 1 ml. Other burner types or special fuel/Oxidant gas combinations are indicated by footnotes. New special techniques (e.g. μl -injection or Pt-loop), which can give an increase in sensitivity by a factor of 10-100 will not be considered.

(b) Electrothermal AAS. The values correspond to an absorbance of 0.025 and assume an absorbance error of ± 0.0025 on the basis of a consumed sample volume of 50 μl . All data were obtained with the Perkin-Elmer HGA-74 graphite furnace with the exception of Hg which was determined by the cold vapour technique.

3. Atomic fluorescence spectrometry (Table 1)

The data assume a sample consumption of 1 ml.

4. Emission spectrography (Table 2)

A sample consumption of 0.1 ml is assumed. Only values corresponding to photographic recording have been mentioned because spectrometric detection which is mainly used in routine analysis depends much more on apparatus parameters and is mostly less sensitive.

(a) Direct current arc. In general a 10-15 A arc (occasionally 20-25 A) was employed as excitation source.

(b) Copper and graphite spark. A condensed spark of 10-20 kV with optimal inductivity to capacity relation was generally employed as excitation source.

5. Emission spectrometry (Table 2)

The data assume a sample consumption of 1 ml.

(a) Inductively coupled plasma (ICP) spectrometry. In general a 27 MHz 1-3 kW generator with

Table 1. L_Q values of some analytical methods (Ref. 1a,2)

Element	Molecular absorption spectrophotometry 3)a)	Atomic absorption spectrometry 4)		Atomic fluorescence spectrometry d)	
	$\mu\text{g ml}^{-1}$	flame b)	electrothermal c)		
	$\mu\text{g ml}^{-1}$	$\mu\text{g ml}^{-1}$	ng	$\mu\text{g ml}^{-15}$)	
Ag	0.1 ⁶⁾ ; 0.05 ⁷⁾	0.07	0.02	0.0004	0.001
Al	0.01 ^{8,9)}	1 ⁶⁷⁾	0.2	0.004	0.5
As	0.05 ¹⁰⁾ ; 0.1 ¹¹⁾	0.2	0.2	0.004	0.8
Au	0.08 ¹²⁾ ; 0.04 ¹³⁾	0.3	0.06	0.001	0.02
B	0.002 ¹⁴⁾ ; 0.004 ¹⁵⁾	45	10	0.2	
Ba		0.5 ⁶⁷⁾	0.8	0.02	
Be	0.01 ⁹⁾ ; 0.05 ¹⁶⁾	0.03 ⁶⁷⁾	0.02	0.0004	0.05
Bi	0.07 ⁶⁾	1	0.2	0.004	0.1
Ca	0.06 ¹⁷⁾	0.08	0.2	0.003	0.1
Cd	0.04 ⁶⁾	0.05	0.006	0.0001	0.0001
Ce	0.2 ¹⁸⁾ ; 0.3 ¹⁹⁾				3
Co	0.05 ²⁰⁾ ; 0.04 ²¹⁾	0.2	0.2	0.004	0.05
Cr	0.04 ²²⁾	0.2	0.1	0.002	0.1
Cs		0.6			
Cu	0.03 ⁶⁾ ; 0.1 ²³⁾	0.2	0.2	0.003	0.005
Dy	0.2 ¹⁸⁾	0.8 ⁶⁷⁾			2
Er	0.2 ¹⁸⁾	1 ⁶⁷⁾			3
Eu	0.2 ¹⁸⁾	0.7 ⁶⁷⁾			0.1
Fe	0.07 ²⁴⁾ ; 0.1 ²⁵⁾	0.2	0.1	0.002	0.04
Ga	0.04 ^{12,26)}	3	1	0.02	2
Gd	0.2 ¹⁸⁾	20 ⁶⁷⁾			
Ge	0.01 ²⁷⁾	3 ⁶⁷⁾			0.5
Hf	0.1 ²⁸⁾	17 ⁶⁷⁾			30
Hg	0.08 ⁶⁾	15	10; 15 ⁶⁹⁾	0.2	0.1
Ho	0.2 ¹⁸⁾	0.8 ⁶⁷⁾			1
In	0.04 ⁶⁾	1	0.8	0.02	0.5
Ir	0.1 ²⁹⁾	13	9	0.2	500
K		0.06	0.05	0.001	
La	0.2 ¹⁸⁾	40 ⁶⁷⁾			
Li		0.05	0.2	0.003	
Lu	0.2 ¹⁸⁾	10 ⁶⁷⁾			15
Mg	0.04 ³⁰⁾ ; 0.1 ³¹⁾	0.01	0.004	0.00008	0.005
Mn	0.2 ³²⁾ ; 0.002 ³³⁾	0.1	0.04	0.0008	0.03
Mo	0.1 ³⁴⁾ ; 0.2 ²⁵⁾	0.8 ⁶⁷⁾	1	0.02	3
Na		0.02	0.03	0.006	500
Nb	0.07 ²⁵⁾ ; 0.04 ³⁵⁾	35 ⁶⁷⁾			8
Nd	0.2 ¹⁸⁾	11 ⁶⁷⁾			10
Ni	0.1 ³⁶⁾ ; 0.02 ³⁷⁾	0.2	0.5	0.01	0.1
Np	0.4 ³⁸⁾				
Os	0.2 ³⁹⁾	1 ⁶⁷⁾			750
P	0.03 ⁴⁰⁾ ; 0.003 ³⁴⁾	500 ⁶⁷⁾			
Pb	0.08 ⁶⁾ ; 0.1 ⁴¹⁾	0.6	0.1	0.002	0.05
Pd	0.02 ⁴²⁾ ; 0.04 ⁴³⁾	0.4	2	0.04	0.2

Table 1. (continued) L_Q values of some analytical methods (Ref. 1a,2)

Element	Molecular absorption spectrophotometry ^{3)a)} $\mu\text{g ml}^{-1}$	Atomic absorption spectrometry ⁴⁾		Atomic fluorescence spectrometry ^{d)} $\mu\text{g ml}^{-1}$	
		flame ^{b)} $\mu\text{g ml}^{-1}$	electrothermal ^{c)} ng $\mu\text{g ml}^{-15)$		
Pm	0.2 ¹⁸⁾				
Pr	0.2 ¹⁸⁾	25 ⁶⁷⁾	3	5	
Pt	0.6 ²⁹⁾	2	3	0.06	2
Rb		0.2			
Re	0.1 ⁴⁴⁾ ; 0.1 ²⁵⁾	17 ⁶⁷⁾			
Rh	0.7 ²⁹⁾	0.5	10	0.2	15
Ru	0.3 ⁴⁵⁾ ; 0.1 ¹⁹⁾	1			3
S	0.01 ⁴⁶⁾ ; 0.02 ⁴⁷⁾				
Sb	0.08 ¹²⁾ ; 0.1 ⁴⁸⁾	1	0.2	0.004	0.3
Sc	0.2 ⁴⁹⁾ ; 0.02 ⁵⁹⁾	0.5 ⁶⁷⁾			25
Se	0.2 ⁵¹⁾ ; 0.08 ⁵²⁾	0.3 ⁶⁸⁾	0.3	0.006	0.5
Si	0.03 ⁵³⁾	5 ⁶⁷⁾	0.5	0.01	3
Sm	0.2 ¹⁸⁾	10 ⁶⁷⁾			0.8
Sn	0.07 ²⁷⁾ ; 0.03 ⁵⁴⁾	0.4 ⁶⁸⁾	0.3	0.006	0.3
Sr		0.2 ⁶⁷⁾	0.1	0.002	0.1
Ta	2 ⁵⁵⁾ ; 0.05 ⁵⁶⁾	35 ⁶⁷⁾			
Tb	0.2 ¹⁸⁾	8 ⁶⁷⁾			5
Tc	0.05 ²⁵⁾ ; 0.2 ³⁴⁾		500	10	
Te	0.1 ⁵⁷⁾ ; 0.6 ⁵⁸⁾	0.7	1	0.02	0.5
Th	0.2 ¹⁸⁾ ; 0.4 ⁵⁹⁾				
Ti	0.1 ⁶⁰⁾ ; 0.03 ²⁵⁾	0.3 ^{67,70)}	200	4	30
Tl	0.06 ¹²⁾	0.6	0.5	0.01	0.05
Tm	0.2 ¹⁸⁾	0.6 ⁶⁷⁾			
U	0.4 ⁴¹⁾ ; 0.1 ⁶²⁾	150 ⁶⁷⁾	0.1	0.002	25
V	0.4 ⁶³⁾ ; 0.04 ⁶⁴⁾	2 ⁶⁷⁾	2	0.04	1
W	0.2 ³⁴⁾	20 ⁶⁷⁾			
Y	0.1 ⁶⁵⁾	2 ⁶⁷⁾			
Yb	0.2 ¹⁸⁾	0.2 ⁶⁷⁾	0.5	0.01	0.05
Zn	0.02 ⁶⁾ ; 0.02 ⁶⁶⁾	0.02	0.003	0.00006	0.0001
Zr	0.7 ^{28,65)}	10 ^{67,71)}			40

Footnotes to Table 1

- a) Reference (2)
b) References (2-5)
c) References (2,3,6-8)
d) References (2,9-54)

Footnotes to Table 1 (continued)

- 1) Compiled by O.G. Koch
- 2) The values are given in $\mu\text{g ml}^{-1}$, i.e. $L_0 [\mu\text{g ml}^{-1}]$ unless otherwise stated. $L_0 [\mu\text{g ml}^{-1}] = L_0 [\mu\text{g}]$ assuming a sample consumption of 1 ml
- 3) Per absorption path length of 1 cm
- 4) Values for air/C₂H₂-flame, without specifying flame composition
- 5) For sample aliquot of 50 μl
- 6) Dithizone
- 7) 1,10-Phenanthroline brompyrogallol red
- 8) Eriochrom cyanine
- 9) Chromazurol S
- 10) Molybdenum blue
- 11) Silver diethyldithiocarbamate
- 12) Rhodamine B
- 13) Methyl violet
- 14) Curcumin
- 15) Methylene blue
- 16) 8-Hydroxyquinoline
- 17) Glyoxal-bis-(2-hydroxyanil)
- 18) Arsenazo I
- 19) 1,10-Phenanthroline
- 0) Nitroso-R salt
- 1) 2-Nitroso-1-naphthol
- 2) Diphenylcarbazide
- 3) Bathocuproine
- 4) Bathophenanthroline
- 5) Thiocyanate
- 6) Hematein
- 27) Phenylfluorone
- 28) Xylenol orange
- 29) SnCl₂
- 30) Eriochrome black T
- 31) 8-Hydroquinoline
- 32) Formaldoxime
- 33) Leucomalachite green
- 34) Dithiol
- 35) Brompyrogallol red
- 36) Dimethyl glyoxime
- 37) Pyridine-2-aldehyde-2-quinolyldiazone
- 38) Thorin
- 39) 1-Naphthylamine-4,6,8-trisulphonic acid
- 40) Molybdenum blue
- 41) 4(2-Pyridylazo)resorcinol
- 42) Pyridine Rose bengal extra
- 43) p-Nitrosodiphenylamine
- 44) α -Furildioxime
- 45) 1,4-Diphenylthiosemicarbazide
- 46) Methylene blue-method
- 47) p-Rosaniline
- 48) Methylfluorone
- 49) Alizarin sulphonic acid
- 50) Eriochrome brilliant violet B
- 51) 3,3'-Diaminebenzidine
- 52) 2,3-Diaminonaphthalene
- 53) Molybdenum blue
- 54) 3'-pyridylfluorone
- 55) Pyrogallol
- 56) Malachite green
- 57) Bismuthiol II
- 58) Tellurium sol
- 59) Thorin
- 60) Tiron
- 61) Dibenzoylmethane
- 62) 2(2-pyridylazo)-5-diethylaminophenol
- 63) Benzohydroxamic acid
- 64) 3,3'-Dimethylnaphthidine
- 65) Pyrocatechol violet
- 66) 1(5-Chloro-2-pyridylazo)-2-naphthol
- 67) N₂O/C₂H₂ flame
- 68) Ar/H₂ flame
- 69) 13,5-cm gas path length cell
- 70) With 5 mg NH₄F ml⁻¹
- 71) With 2 mg HN₄F ml⁻¹

Table 2. L_Q -values ($\mu\text{g ml}^{-1}$) of some analytical methods ¹⁾

Element	Emission spectrography			Emission spectrometry	
	direct current arcs ^{a)}	copper spark ^{b)}	graphite spark ^{2)c)}	ICP	Flame ^{e)}
Ag	0.1	2	0.005	0.02	0.1
Al	0.5	0.1	0.03	0.01	0.05
As	20	5	1	0.2	150
Au	1	0.3		0.1	5
B	0.5	0.1	0.003	0.01	150
Ba	0.2	0.1	0.02	0.0005	0.005
Be	0.05	0.002		0.0005	3
Bi	0.3	0.2	0.05	0.3	150
Ca	0.05	0.1	0.01	0.00005	0.0005
Cd	2	1	0.2	0.005	10
Ce	10	0.5		0.02	50
Co	0.3	0.5	0.05	0.01	0.3
Cr	0.7	0.1	0.01	0.005	0.03
Cs	3	0.5			0.5
Cu	0.05	1	0.005	0.005	0.05
Dy	3	0.5		0.04	0.5
Er	2	0.5		0.01	1
Eu	2	0.03		0.001	0.01
Fe	2	0.8	0.03	0.02	0.3
Ga	0.7	0.5		0.03	0.2
Gd	3	0.3		0.02	20
Ge	0.5			0.05	3
Hf	15	0.5		0.1	250
Hg	20	5	0.1	0.2	50
Ho	2	0.2		0.05	0.5
In	1	1	0.1	0.2	0.02
Ir	5	5		0.5	250
K	5	0.1		0.2	0.01
La	2	0.05		0.01	20
Li	0.2	0.002		0.002	0.0002
Lu	2	0.5		0.05	3
Mg	0.05	0.01	0.005	0.0005	0.1
Mn	0.3	0.03	0.003	0.002	0.02
Mo	2	0.05	0.02	0.01	0.8
Na	1	0.3		0.001	0.002
Nb	0.8	0.2	0.05	0.01	5
Nd	10	0.3		0.02	5
Ni	0.5	0.1	0.01	0.02	0.1
Np		2			
Os	4			0.05	30
P	30	20	0.1	0.2	
Pa		2			

Table 2.(continued) L_0 -values ($\mu\text{g ml}^{-1}$) of some analytical methods ¹⁾

Element	Emission spectrography			Emission spectrometry	
	direct current arc ^{a)}	copper spark ^{b)}	graphite spark ^{2)c)}	ICP	Flame ^{e)}
Pb	2	0.4	0.02	0.02	0.8
Pd	5	0.5		0.05	0.3
Pr	20	0.2		0.1	10
Pt	3	0.02		0.1	15
Pu		2			
Rb	10	0.2			0.03
Re	10	2		0.2	1
Rh	3			0.02	1
Ru	10			0.5	2
Sb	3	5	0.1	0.5	50
Sc	0.5	0.01		0.01	1
Se	100			0.2	500
Si	0.5	0.1		0.03	20
Sm	5	0.5		0.05	2
Sn	0.7			0.1	1
Sr	0.5	0.1	0.02	0.0002	0.001
Ta	50	1	0.1	0.3	50
Tb	10	1		0.05	5
Te	50	3		0.3	500
Th	10	0.5		0.02	400
Ti	0.2	0.1	0.03	0.005	1
Tl	3	2	0.5	0.5	0.1
Tm	3	0.1		0.02	1
U	25	1		0.1	40
V	0.5	0.08	0.01	0.02	0.05
W	7	0.1	0.1	0.02	3
Y	1	0.05		0.001	5
Yb	1	0.05		0.002	0.2
Zn	3	2	0.1	0.005	150
Zr	0.5	0.3	0.03	0.01	20

1) Compiled by O.G. Koch

2) With coated electrodes

a) References (2,50-58, 59-64, 66-72)

b) References (2,55,56,73-75)

c) References (2,65,76,77)

d) References (78-82, 113-122)

e) References (2,79,83-88)

Table 3. L_Q values ($\mu\text{g ml}^{-1}$) of some analytical methods¹⁾

Element	XRF (2,a)	Mass spectro- metry (3,4,b)	Neutron activation ²⁾		Element	XRF (2,a)	Mass spectro- metry (3,4,b)	Neutron activation ²⁾	
			without chemical separation (c)	with separation (d)				without chemical separation (c)	with separation (d)
Ar		(0.0003)	(0.0003)		Ne		(0.0002)	(0,02)	
Ag	4	0.02	0.0002	3	Nb		0.01	0.01	0.5
Al	5	0.002	0.003	50	Nd		0.04	0.05	0.2
As	1	0.006	0.002	0.004	Ni	0.5	0.007	0.1	0.2
Au	2	0.02	0.006	0.001	O		(0.0001)		
B	1 ⁵⁾	0.001			Os		0.04	0.04	0.07
Ba	0,3	0.02	0.01	0.02	P	2	0.003	0.2	0.3
Be	1 ⁵⁾	0.001			Pb	2	0.03	25	50
Bi	2	0.02	5	10	Pd		0.03	0.002	0.005
Br	2	0.01	0.0005	0.004	Pr		0.01	0.001	0.002
C		0.001			Pt	2	0.05	0.02	0.07
Ca	0.3	0.003	0.5	10	Rb		0.01	0.3	0.5
Cd	0.7	0.03	0.03	0.07	Re		0.02	0.0003	0.0006
Ce	0.6	0.01	0.2	0.4	Rh		0.01	0.0002	0.06
Cl	0.4	0.004	0.006	0.03	Ru		0.003	0.2	0.05
Co	0.1	0.005	0.03	0.6	S	1; 0.1 ⁵⁾	0.003	300	600
Cr	0.5	0.005	7	14	Sb	0.08	0.02	0.01	0.02
Cs	0.5	0.01	0.5	1	Sc		0.004	0.03	0.06
Cu	1	0.01	0.005	0.01	Se	1	0.01	0.01	0.05
Dy		0.05	0.0001	0.0002	Si	0.2	0.003	0.2	0.5
Er		0.05	0.006	0.01	Sm		0.05	0.001	0.002
Eu		0.02	0.00001	0.00003	Sn	0.04	0.03	0.5	1
F	1 ⁵⁾ ; 3	0.002	0.06		Sr	1	0.001	0.2	0.4
Fe	1	0.005	140	280	Ta		0.02	0.2	0.3
Ga		0.01	0.004	0.01	Tb		0.01	0.03	0.06
Gd		0.05	0.01	0.03	Te		0.03	0.05	0.1
Ge		0.02	0.01	0.02	Th		0.02	0.001	0.004
H		(0.00001)			Ti	0.2	0.005	0.2	10
He		(0.00003)			Tl		0.02	7	14
Hf	0.7	0.04	0.2	0.4	Tm		0.01	0.02	0.04
Hg	1	0.06	0.01	0.02	U	3	0.02	0.002	0.01
Ho		0.01	0.0003	0.0006	V	0.3	0.004	0.0003	0.2
I	0.2	0.01	0.0005	0.003	W		0.05	0.003	0.005
In		0.01	0.0002	0.0007	Xe		(0.004)	(0.1)	
Ir		0.03	0.0002	0.0004	Y	0.7	0.007	0.02	0.03
K	0.1	0.003	0.03	0.06	Yb		0.05	0.006	0.01
Kr		(0.001)	(0.01)		Zn	1	0.01	0.05	0.2
La	0,4	0.01	0.003	0.006	Zr	0.4	0.01	1	2
Li	1 ⁵⁾	0.0006	0.005						
Lu		0.01	0.0001	0.0002					
Mg	2	0.003	0.02	4					
Mn	0.3	0.005	0.0001	0.0002					
Mo	2	0.03	0.2	0.5					
N		(0.0001)							
Na	1 ⁵⁾ ; 10	0.002	0.003	0.006					

Footnotes to Table 3

1) O.G. Koch and G.H. Morrison

2 & 3) Assumed sample consumption 1 ml (2), 0.1 ml (3)

4) Values in paranthesis in μg

5) Indirect determination after precipitation with trace collect

(a) References 2, 89-106); (b) Reference 107 ; (c) References 2,108-111;

(d) References 2, 112

Table 4. L_Q values of some analytical methods ^{1,2)} in $\mu\text{g ml}^{-1}$

Element	Direct current (3)	Polarography Linear sweep & cathode ray	Pulse	Inverse Voltammetry (17)	Ion-selective electrode potentiometry (4)	Footnotes to Table 4
Ag			0.2	0.00001 ⁵⁾	0.02	1) Compiled by P.D.Lafleur
Al	0.1	0.005 ⁶⁾	0.0001	0.002 ⁷⁾	*	2) Assumed sample consumption of 10 ml
As	0.1	0.02	0.004	0.002 ⁸⁾	*	3) Classical polarography using the dropping mercury electrode
Au	0.5		0.005	0.001 ⁵⁾	*	4) Values given are for direct measurements, elements marked with an asterisk can be determined by indirect methods but limits have not been established
B					1 ⁹⁾	
Ba					0.8	
Bi	0.5	0.05	0.005	0.00001		
Br	10	0.05 ¹⁰⁾	0.0001		0.4	
Ca			0.04		0.5	
Cd	0.2	0.02	0.002	0.00001	0.03	5) Bare glassy carbon electrode of epoxide-impregnated graphite
Cl		1	0.0001		0.5	6) Solochrome Violet RS complex
Co	0.1	0.05	0.003	0.0001 ¹²⁾		7) Adsorption concentration of complex on carbon paste electrode prior to oxidation
Cr		0.1	0.02			8) Au or Cu thin-film carbon electrode
Cu	0.2	0.02	0.002	0.00002	0.01	9) After conversion to BF_4^-
F					0.02	
Fe	0.1	0.005 ⁶⁾	0.003	0.0002 ¹³⁾	0.3	
$\text{H}(\text{H}_3\text{O}^+)$					1×10^{-9}	
Hg	1			0.0005 ⁵⁾	2	
I	10	0.05 ¹⁰⁾	0.0001		0.1	10) As iodate
In	1		0.002	0.00002		11) Normal anodic stripping voltammetry, if not indicated by footnotes; average plating time 10 min
K					0.8	
Li					0.05	
Mg			0.04		0.5	12) Cathodic stripping of oxide on Pt electrode
Mn	0.2	0.1	0.01		*	13) Indirect method involving chemical exchange with bismuth-EDTA complex
Mo	5.0		0.02			
Na					0.01	
Ni	0.1	0.1	0.003	0.02 ¹²⁾		14) Dissolved oxygen; but determination by a galvanic cell is to be preferred
O					0.005 ¹⁴⁾	
Pb	0.4	0.02	0.003	0.00002	0.03	15) Cathodic stripping from a hanging mercury drop electrode
S					0.01	
Sb		0.05	0.004	0.00004		16) Catalytic wave with nitrate
Se	0.5	0.2	0.00002 ¹⁵⁾			17) Average plating time 10 min.
Sn	0.2	0.05	0.003	0.00004	*	
Te		0.02				
Ti	1	0.05	0.008			
Tl	1		0.01	0.00002		
U	0.1 ¹⁶⁾	0.01 ¹⁶⁾	0.01			
V		0.1		0.002 ⁷⁾		
Zn	0.5	0.05	0.003	0.00003		
Zr	2		0.002			
$\text{N}(\text{NH}_3, \text{NH}_4^+, \text{NO}_3^-)$					0.1	

pneumatic nebulizer was used. Using an ultrasonic nebulizer the limit of determination can be improved by a factor of 5-10.

UHF-excitation sources like a microwave induced plasma (MIP) and capacitively-coupled microwave plasma (CMP) are less universal and are associated with more elemental cross-interferences. This is the reason that they have not yet been sufficiently investigated to compile their limits of applicability.

(b) Flame spectrometry. The fuel:oxidant gas combination with the best L_Q value was chosen for each element.

6. X-ray fluorescence spectrometry (XRF) Table 3).

Only wavelength dispersive techniques will be considered. The L_Q values have been calculated for a sample diameter (in general on a paper filter or mylar foil as sample support) of 30-34 mm with a surface of 7-9 cm² assuming a sample consumption of 1 ml with respect to the solution technique, which only will be considered in this report.

7. Spark-source mass spectrography (Table 3)

To calculate L_Q it is assumed that 5×10^{11} singly charged ions are necessary to achieve the photographic limit of detection. The values calculated were corrected for the relative abundance of the principal isotope and further multiplied by 10 to take into account losses of substance during the measurement (a factor of 2), and for converting the detection limit into the determination limit (a factor of 5) and assuming a solution consumption of 0.1 ml. Solid-state mass spectrography will not be considered, because it is less sensitive.

8. Neutron activation (Table 3).

Also in this context the data are only given for solution techniques, assuming a sample amount of 0.1 ml. Non-destructive excitation of a solid sample will in each case lead to worse limits of determination. The values listed are based on the following assumptions using the mode of decay (γ or β) that will produce the best L_Q : viz. a thermal neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, an irradiation time of 10 h, measurements without delay and loss of substance, i.e. without chemical separation, and with chemical separation with a delay of 30 min and a 50 % chemical yield and a detectable counting rate of 120 cpm for β -radiation and 300 cpm for γ -radiation.

9. Electrochemical methods (Table 4)

Among the methods treated in this survey, inverse (stripping) voltammetry is the only method that includes an preconcentration procedure, in the form of the plating (deposition) step. Therefore, in stripping voltammetry the sensitivity and L_Q are directly proportional to the plating time, which, depending on the time available for analysis, could be from less than 1 min to more than 30 min.

This should be considered when comparing the L_Q values for stripping voltammetry with those of the other methods. Mainly the anodic stripping technique is used. Exceptions are the cathodic stripping voltammetric determinations of Co and Se, the conditions of which are indicated by footnotes.

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