Soil Science Division

ACSAD / R 24 / 1979

ANALYSIS OF PLANT MATERIAL

Determination of Co, Cu, Fe, Mn, Zn, by Atomic Absorption Spectrometry

Laboratory Training Manual No. 3
ACSAD training courses on fertility

Damascus - 1979

THE ARAB CENTER
FOR THE STUDIES OF ARID ZONES AND DRY LANDS
(ACSAD)

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- Analysis of Plant Material -

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Damascus
1980

Analysis of Co, Cu, Fe, Mn, Zn
In Plant Material by Flame AAS

Contents:

Introduction

The present paper deals with technical aspects of flame atomic absorption spectrometric measurements of some micronutrients in plants. These elements are presently determined on a routine basis in many laboratories but nevertheless their determination is not free of problems especially to newcomers in the field of AAS. Our purpose is to facilitate the approach of analytical work by presenting a survey of data made available by existing collaborative studies and inter-laboratories cross-checking of methods. In a first part are presented preparation of samples and ashing technique which have been recorgnized to be the simplest and the safest. Then, for each element are described the AAS instrument variables which are the parameters on which depend the signal of the instrument. It has to be born in mind that each instrument has its own characteristic. Each one is provided with a manufacturers cook-book describing for each element the optimum values of the instrument settings. It should be said that optimum values represent a compromise between requirement which differ from one user to another and are not necessary the best ones in a particular problem. They represent the safest approach at an initial stage, but the analyst can make systematic improvements of the performance of his instrument by knowing the effect of each adjustment on signal reading.

For each element are given, for the main line and the most common flame, (the first listed under "flame" heading) the characteristics of the curve ; detection limits (d.l), sensitivity (s), concentration giving 100 milliabsorbance (d 100), maximum concentration corresponding too lincar calibration (m).

Secondary lines are given for information, for in trace elements, the most sensitive line is invariably the only suitable one.

Interferences are listed only for the salse of drawing attention on possible problems to be expected. It is of prime importance to know that interferences are matrix-dependant, and that no general mathematical formulation is possible at the present stage of knowledge. There are few ways of diminishing suspected interferences (addition of releasing agents, ionic buffer, stoechiometry of flame ...) but in no case, it should be omitted to compare results by running a standard of similar composition to unknown .

Finally some data on precision of AAS measurements are presented. They will help the analyst to evaluate the quality of his results as compared to those of experienced laboratories working on similar material.

Definitions of terms used in AAS litterature are listed in paragraph 7. A selected bibliography, choosed among more than a thousand papers published every year on atomic absorption ends these short coments on Co, Cu, Fe, Mn and Ni determination in plant material.

I. PREPARATION OF SAMPLES

1. Cleaning

As soon as possible after they have been collected, plant organs are washed few seconds with 1% solution of Teepol, immediatly rinsed three times with deionized water and dried for 24 hours at 65°C. Samples are then dried two hours at 100°C, and finely grinded. A fineness of about 0,2 m/m is sufficient to insure a representative sample in most cases without mechanical losses during weighing and ashing.

It is a safe practice to use a grinder fitted with a different bowls and heads for each sample, or to thoroughly clean the grinder between samples to avoid contamination-domestic coffee mixer-grinders have been found convenient and inexpensive for this use.

2. Digestion

The following method is the official one adopted by the " Comite Interinstituts pour l'etude des plantes par le diagnostie foliaire " in Europe.

- Dry the finely ground material (less than 0,2 m/m) for 16 hours at 70 - 80°C.
- Cool 30 min. in a dessicatior
- Transfer 2g in a platinum capsule
- Place the capsule in a cool furnace, raise temperature to 450°C over at least three hours, (the raise between 250° and 300° on one hand and 360° to 450° on the other hand has to be done more slowly).

- Maintain at 450° for two hours. Cool away from air drafts
- Moisten the ash, which should be whitish, by 2 ml dist water and about 2 ml HCl; heat until fumes appear.
- Filter on ashless filter paper into 100 ml graduated flask
- Fince 3 times with 5 ml warm water (30 - 40°)
- Allow to drain completely , fold the filter paper, ignite it in tis original capsule for 30 min. at 550°C max.
- Take up in 5 ml hydrofluoric acid
- Heat to dryness gently on hot plate, not exceeding 100°C
- Take up in 1 ml conc. HCl
- Transfer to the 100 ml vol. flask rince the platinum crucible make up, to the mark.

This solution is convenient for determination of Ca, Mg, K, Na, Fe, Mn, Cu, Zm, ... and phosphorus.

Note 1: Finely ground plant material being rather hydrocscopic, the weighing should be rapid, it is recommented to weight quickly but accurately any weight from 1,8 to 2,2 gr and to apply the necessary correction factor to the result during calculation of results.

Note 2: Contamination of sample occurs mainly during the preparation and digestion of sample, (MIZUIKE, PINTA). For this reason, and because the final accuracy of results depend greatly on a good mineralisation, it is recommended to assigh a skillfull technician to this task.

Note 3: A reagent bank and a standard sample of known composition are run together with every batch of samples.

II. INSTRUMENT PARAMETERS

1. Copper
2. Cobalt
3. Iron
4. Manganese
5. Zinc

- Copper -
Cu

n = 59	f(Cuo/Cu) = 1,251	* Ei = 7,72
m = 63,646	1/f = 0.798	* Do = 4,9

Introduction: If concentration in plant is higher than 6 ppm, no concentration step is needed and direct reading may be used.

Absorption:

Stock Solution: for 1000 ppm Cu prepare:

- 1,000 gr metallic Cu dissolved in 3 ml conc. HNO_3. Adjust to 1l.
- 3,929 $CuSO_4$, $5H_2O$/l.
- 3,798 gr Cu (No_3), $3H_2O$/l. The latter solution should be standardized by complexometry.
- Organic Solutions:-from Bis (1 phenyl, 1-3 butanediono) Copper II.
  -from copper - Cyclohexanebutyrate.

Lamp Current:

- Maximum precision : 60-80% of max. lamp current
- Maximum sensitivity : 40-50% of max. lamp current
- Optimum : 60 % of max. lamp current

Flame: Air/Acet. stoechiometric or lean
Air/Prop. gives a better sensitivity (50 to 100% increase of the signal as compared to Air/C_2H_2).

Burner height:

- Average of 11 m/m in Air/Acet. stoechiometric flame and single slot premix burner (asp. rate 4-6 ml/min.) Burner height affects the stability of the signal and linearity of the standard curve.

Ei :
Do :

Main line characteristics concentrations: (cf. definitions chap.V)

- 324,75 nm (not a resonance line)

  dl = 0,006 s = 0,06 d_{100} = 1 m = 4 to 6

Table of Lines:

Wavelength (nm)	r.s	range (ppm)	Energy levels (cm^{-1})	Reson. Line	f	band-pass (nm)
324,75	1	0.06-6	0-30784	No	• 0.74 + 0.62	0.5
327,40	1/2	-	0-30535	Yes	+ 0,38	0.5
217,89	1/5			No	+ 0,011	0.3
218,2	1/5			No		0.3
216,51	1/6					0.3
222,57	1/15		0-44916	No	0,004	0.15
249,22	1/100		0-40114	No	-	0.5
244,16	1/300	0-40944				1

Interferences:

- A very large excess(more than 3000 ppm) of transition elements give a depressed reading.
- Virtually no other interferences in Air/Acetylene flame.

Signal:

One of the better of all elements. The signal is used to calibrate instruments and detecting noises which are instrument-dependant.

• Landolt : Oscillator Strength

\+ Price : " "

Enhancing solvents: (Allan 1961)

- When compared to an aqueous solution the following enhancement factors are obtained:

40% Acetone, 20% isobutanol : 2.3
8% Acetone : 3.5
MIBK : 4 (independantly of any extraction factor)
Ethyl-Acetate : 5

Emission: Main Line 327,40 : max. sensitivity
Sec. Line 324,70 : less sensitive

Both lines have to be used in conjonction with the minimum bandpass and max. photomultiplication.

Flame: N-oxide/acet. Lean (best sensit.)
Air/Acet. Steoch (less sensit.)

Extraction Systems:

- APDC/MIBK (Allan - Fishman - Trent)
- APDC/Etylamine Ketone

Cu is used to check the completeness of extraction prodedures (Allan).

Concentration in nature: (in ppm)

- Soils : - General range: 2-200
  - Dry Lands : 0.01-0.02 (mean 0.04)
- Plants: - General: 1-25 (AUBERT-PINTA)
  - Mais : 1,5 to 7,5 (RAZMILIC)
- Waters: - Drinking : max.: 1 ppm
  - Irrigat. : max.: 0.5 ppm

Precision:

- SINGH (19770 reports a relative standard deviation varying from 20 to 30% for six differents plants analysed by ten different laboratories.

- PINTA (1974) reports a relative standard deviation varying from 4 to 20% on different plant materials (ten different samples) analysed by seventeen laboratories using the CII method presented in this paper.

- The measurement itself, as appreciated by the r.s.d of ten successives peaks obtained at close interval without modefying instrument parameter is around:

  1% at 500 mA level
  2% at 1500 mA level

Comparison with other methodes:

- The respective usual sensitivities of AAS, Molecular Absorption (MA), Polarography and Flame Emission Spectrometry (FE) are:

  M.A : 0.02 (ppm)
  AAS : 0.05 (ppm) Dithiocarbamate
  POL : 0.4 (ppm)
  F.E : 0.5 (ppm) (327,4 mm)

2 - COBALT -

Co

n = 27 $f(Co\ o/Co) = 1{,}2714$ Ei = 7,86

$1/f = 0{,}7864$

Introduction:

A concentration of 0.3 ppm in dry material of plant gives 0.003 microgram per ml of solution (1 gr of plant being ashed and digested in a final 100 ml volume). This value lies for below the defection limit of flame AAS. A preconcentration will be necessary. This first step is described in the litterature given at the end. The data given below refer to aqueous solution, independantly of any preconcentration step.

Absorption:

Stock Solution: a 1000 ppm Co solution is given by:

- 1,000 gr of fine metal dissolved in a minimum of conc. HCl
- 4,038 gr of $CoCl_2$, $6H_2O$/1
- 4,937 gr of Co $(No_3)_2$/1

Since both these salts are highly hygroscopies, check titration by complexometry is necessary.

Lamp Current: depends on analytical line:

- 240,72 nm: the decrease of sensitivity with lamp current being sharp, a low current must be used for best sensitivity.
- 242,49 nm: the sensitivity decreases only slightly as lamp current is raised, therefore a high current (80% of max. permissible) should provide both good sensitivity and good precision.

- For most medium intensity Co hollow cathod lamp, the photon noise is as great as the lamp fluctuation noise.

Flame: - Air/Acet. : stoechiometrie - (the most stable)
- Air/Acet. : reducing (the most sensitive)
- Air/Propan. : reducing
- N-oxyde/Acet: gives better results than other combinations either in AA or in Fe mode.

Main Line:

1. 240,725 nm (minimum bandpass for low concentrations)
   - For low concentration of Co this is the best line but strong curvature appears after 5 ppm due to the impossibility of isolating other neighbouring lines.

   Characteristics: $dl = 0.03$ $d_{100} = 1,5$
   $s = 0.1$ $m = 5$

2. 242,493 nm (medium bandpass). This line is used for higher concentrations.

Secondary lines:

Line nm	r.s.	range mgr/l	energy levels cm-1	Reson.	f	band-pass nm
242,493	0.8	2-50	0-41226	No	0.19	
241,46	0.5	1-100	816-42269	No		
252,136	0.3		0-38649	No	0.19	
243,58	0.3					0.5 nm
304,40	0.08					
• 352,685	0.06	100-2000	0-28346	Yes		
346,580	0.03					0.15
341,263	0.03					0.15
347,402	0.02					0.15
301,76	0.01					0.5
391,0	0.005					

Interferences:

- Non specific absorption around the main line (240 nm) is corrected either by background correction or by measuring non specific absorbance at 238,8 nm and "Substracting" it from the final result.
- No noticeable interferences in diluted solutions.
- Interferences of Fe, Ni, Ca in high concentration (1500 ppm Ni produces a 50% decreases in the signal (Pinta).

Characteristies of the signal:

- Noisy and extremely dependant on flame and HCl settings.

Enhancing solvents:

- 1% Fe solution in 5% $HClo_4$ produces an 25% increase in signal at 10 ppm level (Pinta).
- 70% isopropanol is a solvent doubling sensitivity for the 240,73 nm line.
- Ethyl. propionate increases sensitivity 50 times (Sachdev).

Emission:

- Main line: 345,35 nm sensitivity: s = 0.5 ppm
- Flame : Air/Prop. (best flame)
  : N-oxyde/acet. (2 m/m red feather only)

Extraction procedures:

- MPDC/MIBK (Brooks - Burrel - Fishman - Sprague)
- 2 Nitroso - 1 Naphtol/Chloroform/MIBK (Simmons)
- 1 Nitroso - 2 Naphtol/Methanol/MIBK (Binnerts)
- Dithizone -/Ethyl-propionate (Sachden)

Concentration in natural products (ppm)

- Soils : General : 1 - 40 (average 4 - 6)
  Dry lands : 0.01 - 0.14 (mean 0.06)
  Ultra basic:
- Plants: General : 0.01 - 1
  Animal feed: 0.05 - 0.5

Precision - Accuracy:

- The same solution passed 10 times in the system at close internals shows a minimum relative standard deviation of:

  0.5% at 500 m Abs. level
  1.0% at 250 m Abs. level

- Relative standard deviation of six replicates using complexation, with 0.5% ethanolic solution of 2 nitroso, 1 naphtol extraction with chloroforus and transfer in MIBK vary from 1.7% (0.08 ppm level) to 9.6 (0.0 ppm level) in wheat and yellow lupin (SIMMONS).

Comparison with other methods: (sensitivities given in mgr/l)

- Atomic Absorption	0.1
- Molecular Absorption	0.05 (Nitroso-R-salt)
- Polarography	1.0
- Flame Emission	0.5 (345,4 nm)

3 - Iron -

Fe

Fe	n = 56	m = 55,847	f(Fe_2O/Fe_2) = 1,429	1/f = 0.299
			f(FeO/Fe) = 1,286	1/f = 0.7773

Stock solution (1000 ppm Fe)

- 1,000 gr pure Fe in 5 ml HCl conc. (add. few drops of MNO_3 conc.); adjust to 1 l.
- 7,021 gr $(NH_4)_2$ Fe $(SO_4)_2$, $6H_2O$, dissolv. adj. to 1 l.
- 4,840 $FeCl_3$, $6H_2O$/1, control Fe concentration by complexometry.
- Organic: Tris (1-phenyl 1,3 butanedione) iron III.

All stock solution must be kept in a dark place in polythene container.

Lamp current:

- max. precision is close to max. current.
- max. sensitivity is 70% of max. current.(For precision work one shall use the maximum lamp associated with the minimum slit width which can be used without the photon noise becoming dominant).

Flame:

C_2H_2/Air Lean (make the yellow fringe just disappear).

Reducing flame gives maximum sensitivity but also max. interferences.

Main Line: 248,327 nm

dl = 0.01   s = 0.1   m = 5.10   (for 0.2 nm bandpass)

This line is used in conjonction with the smallest bandpass possible.

Increasing the slit width leads to loss of sensitivity due to neighbouring non absorbing lines.

Table of Lines:

Wavelength (nm)	r.s.	range ppm	energy levels cm^{-1}	Reson. Yes/No	f	Optim. bandpass nm
248,327	1	1-15	0-40.2570		0.34	0.2
248,819	1/2	2-20	416-40.594	No	-	id.
252.285	1/2	2-20	0-39,626	No	0.30	id.
271,902	1/3	2-20	0-36.767	No	0.15	relat.large
302,064	1/4		0-33.096 416-33,507		0.08	
252.74	1/5		416-39.970	No		
371,994	1/8	10-100	-	-	0.01	0.3 nm very stable
269,69	1/9	-	-	-	-	-
385,991	1/12	-	-	-	0.034	0.3 nm doublet
344,06	1/100	-	-	-	0.055	-
392.03	1/250	-	-	-	-	0.3 -

Interferences:

- Especially from Si and PO_4, in C_2H_2/air flame. This chemical interference is depending on instrument settings and is reduced by increasing flame temperature (enriching in air).
- With C_2H_2/Air oxydant (very lean), Fe interferences are decreased but sensitivity is reduced.
- Interference of Si may be overcome by using a 0.2% $CaCl_2$ sol. as internal ~~corrector~~ (see annex), or by using the hotter C_2H_2/N_2O flame.

- No interference from:
    - 3000 ppm, Ca
    - 1000 ppm, Mg, So$_4$, Cl, transit metals.
    - Interference of Sodium is reported by some authors
- Background correction is necessary for 248,81 line.

Emission:

- **Line** : 371,99 (minimum slit-width and max. photomult.)
- **Flame:** C_2H_2/N_2O Lean (red feather 5 m/m)

Concentrations in Nature :

- **Soils** : from ppm to 70% (as Fe_2O_3) in laterites
- **Water** :-Surface : less than 1 ppm (alcaline waters)
  -Underground : 1-3 ppm
  -Drinking water: 0.1 to 0.2 depending local regulations.
- Plants:-Range: 0.5 to 1000 ppm (maximum frequency between 100-250 ppm) (PINTA).
  -Mais : 6.2 to 24.6 in Mais (RAZMILIC).

Precision:

a. Minimum standard deviation (WEIR - KOFLUK)

- The same liquid sample is nebulized in the same instrument without modifying instrument settings (which are supposed to be optimum).
- Rel. stand. deviation is: - 0.2% at 500 milli abs. level
  - 0.5% at 250 milli abs. level
  - 0.5% at 750 milli abs. level

b. Reproductivity: (BROWN - SKONGSTAD - FISHMAN)

- Three different laboratories using air/acetylene at 248,3 nm found a relative standard deviation of 6,6% at 0.39 mgr/l level, when analysing the same water sample, (BROWN - SKONGSTAD - FISHMAN).

c. Inter-laboratories variation:

During inter-laboratories tests made on plant material, the following results are reported:

	n	p	r-s-d	Concentration (ppm)
SINGH :	10	6	11 to 20%	unknown
PINTA :	18	12	6 to 15%	9 to 1100

n representing the number of lab.ratories analysis p differents plant standard sample. The 18 laboratories of the second line using the same CII method of sample preparation.

Comparison with other methods: (sentivities)

AAS :	0.1	ppm	
M.A :	0.05	ppm	
POL :	1.0	ppm	ortho - phenanthroline
F.E :	0.5	ppm	(371,99 nm)

4- Manganese -
Mn

Mn n = 12 A = 54,938 f(MnO/Mn) = 1,2912 1/f=0.7444 Do=4

f(Mn_2O_3/Mn) = 1,4360 1/f=0.6960 Ei=7,43

<u>Introduction</u>: Mn can be generally determined in plant without extraction or pre-concentration step.

<u>Absorption</u>:

<u>Stock solutions</u>: for 1000 ppm Mn:

- 3,607 gr $MnCl_2$/l or 3.076 gr/l $MnSO_4$, $4H_2O$ in water.
- 1,000 gr metallic Mn in minimum conc. HCl, complete with water to 1l.
- Organometallic: Mn - cyclohexanebutyrate.

<u>Lamp Current</u>:

Sensitivity deesn't change too much with lamp current therefore current should be set to the value giving the best precision (80% max. current).

<u>Flame</u>:

- C_2H_2/air: Reducing (best sensitivity, but also max. interferences).
- C_2H_2/air: Oxydizing (best precision).
- C_3H_8/air: Best stability (without noticeable loss of sensitivity).
- C_2H_2/N_2O: Lean, 5 m/m red feather, suitable for 403,08 nm.

Burner height:

5 to 8 m/m for C_2H_2/air oxidizing.

Main Line: 279,482 nm (0.15 nm bandpass)
dl = 0.005 s = 0.05 (air/acetylene)

Select the minimum possible bandpass to isolate the triplet 279,48 - 279,83 - 280,11 .

Triplet: 279,48 - 279,83 - 280,11 (bandpass 0.7 nm)
dl = 0.002 1 = 0.1

The three lines of the triplet having the same sensitivity it is possible to use the three of them together without the usual loss of linearity, (bandpass 0.7 -0.8 nm).

Table of Lines:

Wavelength (nm)	r.s	Energy levels (cm^{-1})	Range (mgr/l)	
279.482	1	0 - 35770	1 - 10	
279.482	1	0 - 35726	1 - 10	
280.108	1 to 1/2	0 - 35696	2 - 20	
403,976	1/20	0 - 24802	10- 100	Narrow bandpass
222,2	1/50	-	-	too far in UV.
321.70	1/2000			

Interferences:

- Si even in low concentrations; correction by addition of 50 to 2000 ppm $CaCl_2$ to standard and sol.(PLATTE & MARCY).
- Phisphate perchlorates, transition metals (Fe in excess of 25 ppm), in reducing flames .
- No interference of 1000 ppm from Na, K, Ca, Mg.

- After addition of 200 mgr/l Ca, no interference of 1000 ppm sulfate, chloride, phosphate, nitrate, nitrite, bicarbonate, silica, EDTA, Ni, Zn, Cr, B, Pb, Mg, Na.

Emission:

403,08 nm using a lean $C_2H_2/N\ O$ flame.

Addition of Ca in plant material is generally unecessary, since Ca concentration is usually 200 times more than Mn. Emission is as sensitive as absorption.

Concentration in nature: (as ppm)

- Soils : 0-1% (MnO)
- Plants: - range : 5-5000 ppm
  - grasses: 50-300
  - Mais : 6-10 etc...
- Water : - surface :less than 0.5
  - drinking:less than 0.1

Comparison with other methods: (comparison of sensitivities in ppm)

- Atomic Absorption : 0.02
- Molecular Absorption : 0.2
- Polarography : 0.4 (Mno_4)
- Flame Emission : 0.05

Precision:

- Analysis made on the same water samples, on different apparatuses by 18 laboratories given a relative standard deviation of 15% at the level of 0.30 mgr/l.
- Analysis made by ten laboratories on six plant samples gave coefficient of variation lying between 10 and 20% (SINGH).
- CII method applied by 18 laboratories on 12 standard plants gave variation coefficient ranging from 3 to 8.5 for concentrations ranging from 60 to 650 ppm, (PINTA) .

- Zinc -

Zn

Zn n = 38 A = 65,37 f(ZnO/Zn)=1,2447 1/f=0.8034 Do = 4

Ei = 9,39

Absorption:

Stock solution: 1000 ppm

a. 1,000 gr Zn dissolved in 3 ml of conc. HCl, adjusted to 1 l.

b. 1,245 gr ZnO, few drops of water, dissolved in diluted HCl, adjusted to 1 l.

c. Zn - cyclohexanebutyrate.

Lamp Current:

- sensitivity decreases sharply as lamp current increases.
- max. sensitivity 50% max. lamp current.
- max. precision 80% max. lamp current.

Flame:

- C_2H_2/air: Reducing (fuel rich), or stoeck. (no difference in sensitivity by changing the ratios of gases).
- C_3H_8/air: (flame absorbing), more sensitive than C_2H_2/air.
- Caution : Flame absorption noise is important at low wavelength (flame noise becoming much greater than lamp noise). It is therefore important to shield the flame from air-draft.

Burner geight:

6 m/m for C_2H_2/air flame.

Main Line:

213,86 nm (min. bandpass to exclude the 213,60 line of Cu, always present in HCl emission.

s = 0.02 ppm m = 1 ppm d_{100} = 0.5 ppm

(Data given for isopropanol 50% and C_3H_8/air flame).

Table of Lines: (Zn exhibits very few lines)

Wavelength (nm)	r.s	range (ppm)	energy levels	f	band-pass	Res.
213,86	1	0.5 - 10	0-32502	1.2	Minim.	
307,6	1/1000		0-46745	0.00017		Yes

Interferences:

- With elements found in plants no interference occurs in air/ acet. flame.
- More than 500 ppm Si or Al interferes.
- Effect of Sulfuric and perchloric acid is diversely reported matching concentrations of standards and samples is a good precaution.
- Non specific absorption of the flame may be corrected by measuring the absorption at 228,8 nm wavelength of Cadmium.

Enhancing solvents:

- 50% isopropanol.

Emission:

- 213,86 m/m (minimum bandpass)
  Flame N_2O/C_2H_2

Precision:

- The best range for measurement is 250 - 500 milliabsorbance. The following characteristics are reported.

a) For the same solution, same apparatus, same adjustments, the relative standard deviation (r.s.d) of ten consecutives measures is: (WEIR - KOFLUK)

- 0.75% at 500 mA level
- 1% at 250 mA level
- 2% at 750 mA level

b) For the same solution, different instruments in 19 different laboratories, using 213,8 nm line and Air/Acetylene flame.

r.s.d = 25% at 0.112 mg/l level .

c) For the same ten plant samples prepared by 11 different laboratories, using the same technique of ashing, PINTA reports a r.s.d ranging from 6 to 20% for concentration ranging from 12 to 125 ppm.

d) SINGH reports an inter-laboratories order of variations lying 11 to 20% for six cross-checks made by ten laboratories on the same plant material.

Comparison with other methods, (sensitivities given as ppm are compared) :

- Molecular Absorption:	0.01 (dithizone)
- Atomic Absorption :	0.02
- Polarography :	0.2
- Flame Emission :	50 - 100 (213,9 nm)

III. PRECISION OF RESULTS

1- Definitions

2- Evaluation of Individual Errors

3- Precision of Plant Analysis in AA Spectrometry

   A- Intra-Laboratory Characteristics

      a- Final Analytical Result (r.s.d_0)

      b- Preparation of Sample (r.s.d_1)

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   B- Inter-Laboratories Characteristics

      a- Final Analytical Results (R.S.D_0)

      b- Preparation of Sample (R.S.D_1)

III. PRECISION OF RESULTS:

1. Definitions

During the course of an analytical procedure, each step is a source of an individual error. The resultant total error is the statistic sum of individual ones.

We suppose that each step of analysis leads for each sample to a partial result expressed as a number x. We also assume that when n samples are submitted to the same treatment, results x_1, x_2, x_3 ... x_n are normally distributed around a mean value $\bar{x}$. Then, s being the estimate of the standard deviation and $\bar{x}$ the mean value, we express the precision as $100s/\bar{x}$ (relative standard deviation or r.s.d). Providing a sufficient number of measures, s and $\bar{x}$ are constants for a given population. Should one parameter of the population change, s and $\bar{x}$ will change also and we have to consider the population as being a second one. Each population is represented by three numbers: r.s.d $(x , \bar{x})$.

2. Evaluation of individual errors

For each analytical process we may define a finite number of steps, each one being associated with an individual error. The may be listed according to the increasing value of their r.s.d :

1- Final analytical measurment
2- Preparation of sample
3- Sampling

Each step being in turn divided into several ones; for instance : step 2 may be divided into sieving-digestion-evaporation-extraction ...

The conclusions reached apply watever the number of steps.

3- Precision of plant analysis in AAS:

A-Intra-laboratory characteristics

a- Final analytical results : (r.s.d_0)

When the same solution is passed n times through the same AAS spectrophotometer under optima conditons, the smallest value possible of r.s.d is around 0.5%, the following general rule applies:

At the level of 500 milliabsorbance (optimum):

- r.s.d_0 0.5% is excellent
- r.s.d_0 1-1.5% is normal
- r.s.d_0 2.5% and more is poor.

These values differs only slightly from one element to another one:

Ex: 1. Fe:

r.s.d_0 = 0.2% at 500 mA
r.s.d_0 = 0.5% at 250 mA
r.s.d_0 = 1.0% at 1000 mA

2. Mn:

r.s.d_0 = 0.25% at 25 ppm over 100 consec. determination, (Perkin Elmer information, No. L-445).

3. Zn:

r.s.d_0 = 0.75% at 500 mA
r.s.d_0 = 1% at 250 mA
r.s.d_0 = 2% at 750 mA

b- Preparation of sample ($r.s.d_1$):

The same(standard) sample being prepared by the same standard method in the same laboratory, and passed n times through the same AAS spectrophotometer under optimum conditions:

Cu - $r.s.d_1$ = 5% (150-500 milliabsorbance, n greater than 20 CII direct method)

Cu - $r.s.d_2$ = 6.2% (150-500 mA, n = 18 - CII ashing, followed by solvent-extraction).

These values are from Laporte, Kovaesik, Bellanger (op.cit).

c- Sampling:

Not suprisingly, few data are available from the litterature. The r.s.d value of sampling step depends on so many factors that no data are of general use. Furthermore the "True Value" is not easy to define at this stage.

B- Interlaboratories characteristics

a- Final analytical results:

The same sample is analysed by the same method by different laboratories using the same technique but different equipment:

Values reported for $R.S.D_0$ differs from one element to another. The following values have been reported. (BROWN - SKONGSTAD - FISHMAN).

- Iron : R.S.D$_0$ (n= 3 c=0.39 mgr/l) = 6.6%
Manganese: R.S.D$_0$ (n=18 c=0.30 mgr/l) = 6.7%
Zinc : R.S.D$_0$ (n=19 c=0.112 mgr/l) = 25%
Copper : R.S.D$_0$ (n=19 c=0.119 mgr/l) = 39%

b- Preparation of samples:(R.S.D$_1$)

The same standard sample is analysed by the same method by different laboratories .

(Results from PINTA and 24 Europeens laboratories grouped in "Comite Inter-institut des techniques analytiques de diagnostie foliaire, C.I.I).

Copper:

Plant	R.S.D$_1$ %	Level ppm	Number of det. n
Codia discolor	22,6	4,8	12
Artichoke	17,3	7	12
Coton	9,6	15	12
Olive tree (leaf)	6,8	36	12
Apple cox's(leaf)	17,5	177	17
Grape (leaf)	10	886	17

Mn :

Plant	R.S.D$_1$ %	Level ppm	Number of det. n
Apple golden	10,3	47	19
Apple Cox's	4,4	136	18
Eucalyptus	5,5	569	17

Fe :

Plant	R.S.D_1 %	Level ppm	Number of det. n
Codia discolor	8.1	88	16
Palm tree	6.2	199	16
Orange	6.9	465	17
Apple Cox's	11	1154	16

Zn :

Plant	R.S.D_1 %	Level ppm	Number of det. n
Codia discolor	12.4	11	11
Mais	12.6	28	11
Orange	9.6	68	16
Coton	9	125	11

Most values of R.S.D_1 lie between 5 and 15% .
When the same sample is analysed by different laboratories using different methods a much higher value of relative standard deviation, may be expected (perhaps 10 to 30%).

There are few remarks of interest for the analyst:

- Horizontal variation diminishes as the analysis preceeds from sampling to final result, the precision being better at the end. On the contrary, accuracy is more and more difficult to reach as the analytical process is runing. The reason is the increasing difficulty of locating systematic errors.

IV. STANDARD SAMPLE

- Olive (leaf)
- Orange (leaf)
- Palm tree (leaf)
- Peach (leaf)
- Apple Golden (leaf)
- Apple Cox's (leaf)
- Grape (leaf)
- Artichoke (leaf)
- Cotton (leaf)
- Eucolyptus (leaf)
- Hevea (leaf)
- Maize (leaf)

It is common practice to run together with unknown sample a standard sample . This practice is used not only to optimize instrument settings, but also to detect unexpected changes occuring during treatment of samples.

Furthermore when the same standard sample has been analysed a sufficient number of time (at least 20) it may be used to prepare standard curves by successive dilutions. Interferences due to matrix effects are suppressed for sample having similar relative composition .

This chapter gives some data collected by twenty official laboratories in Europeen countries grouped in " Comite Inter-institut d'Analyse Foliaire " (cf. PINTA).

The following table presents some results obtained by official laboratories on standard material available from C.I.I.

Plant	N%	P%	K%	Ca%	Mg%	Fe (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)
Artichoke N	18	19	20	18	20	17	12	17	11
mean	1.970	0.154	0.989	2.974	0.400	323	7.6	111.0	16.2
S	1.13	0.009	0.114	0.147	0.022	29.9	1.32	8.1	3.2
Cordia discolor N	17	17	19	19	19	16	12	18	11
mean	0.7	0.02	0.366	0.83	0.28	88	4.8	654	11
S	0.07	0.004	0.03	0.04	0.01	7.2	1.1	25.0	1.4
Cotton N	17	19	23	22	22	19	12	18	11
mean	3.8	0.36	1.82	3.08	0.41	417	15	218	125
S	0.15	0.02	0.07	0.19	0.02	34.7	1.4	11.3	11.4
Eucalyptus N	18	19	20	18	20	17	12	17	11
mean	1.34	0.08	0.69	1.57	0.20	102.7	8.1	570	12.8
S	0.1	0.009	0.06	0.113	0.017	8.23	1.27	31.8	2.4
Hevea N	17	19	23	22	22	19	12	19	11
mean	3.36	0.26	0.94	1.07	0.33	159	15.4	160.5	39.9
S	0.07	0.01	0.05	0.08	0.02	24	2.4	7.6	2.5
Maize N	17	17	19	19	19	16	12	18	11
mean	2.06	0.22	1.90	1.12	0.36	259	11.8	66	28
S	0.09	0.01	0.11	0.06	0.01	17	1.6	5	3

N = Number of Laboratories, (each one giving one result)

Plant	N	P	K	Ca	Mg	Fe	Cu	Mn	Zn
Olive N	17	19	23	22	22	19	12	19	11
mean	1.36	0.08	0.51	2.60	0.31	171	36	49	16
S	0.09	0.005	0.06	0.13	0.007	19	2.5	4.2	1.2
Orange N	18	19	20	18	20	17	17	17	16
mean	2.38	0.15	1.54	4.88	0.32	465	8.5	75.1	68.5
S	0.12	0.01	0.13	0.17	0.02	32	1.2	5.2	6.6
Palm N	17	17	19	19	19	16	17	18	16
mean	2.67	0.16	0.88	0.80	0.30	200	8.7	630	23
S	0.11	0.06	0.06	0.03	0.01	12.3	1.71	27.7	3.1
Peach N	15	18	19	19	20	18	17	8	16
mean	4.2	0.29	2.18	2.16	0.47	299	15	83	28
S	0.24	0.01	0.12	0.11	0.02	40	2	5	4
Golden N	15	18	19	19	20	18	17	19	16
mean	2.25	0.16	1.44	1.28	0.29	311	8.4	47	30
S	0.12	0.007	0.07	0.08	0.02	34	1.5	4.8	4.3
Cox' N	17	17	19	19	19	16	17	18	16
mean	2.05	0.18	1.04	2.1	0.29	1154	177	136	77
S	0.08	0.07	0.09	0.08	0.02	126	31	6	7.7
Grape N	17	19	23	22	22	19	17	19	16
mean	2.81	0.21	1.22	2.58	0.28	272	885	193	74
S	0.1	0.01	0.07	0.14	0.02	33	93	10	7.4

Note: Original data comprises more complete statistics (median, normality of the distribution ....) see PINTA, Etalons vegetaux pour l'analyse foliaire ANALUSIS, 3 - 6 - 1975 .

V. DEFINITIONS

- Absorbance
- Absorption percentage
- Accuracy
- Amplifier read. out noise
- Background correction
- Bandpass
- Curve correction
- Dark - current noise
- Detection limit
- Dissociation energy (oxyde)
- Energy level
- Flame transmission noise
- Geometrical slit width
- Interferences
- Internal standard
- Ionization potential
- Lamp flicker noise
- Mean value
- Noise
- Multi-element lamp
- Oscillator strenght
- Photomultiplier
- Photon noise
- Precision
- Reciprocal linear dispersion
- Relative sensitivity (sec.lines)
- Repeatability
- Reproducibility
- Resolution
- Resonance line
- Rich (lean)
- Sensitivity
- Standard addition
- Standard deviation
- Stoechiometry of flame
- Variance

Absorbance (A):

Decimal logarithum of the ratio of the radiant power incident on the sample to the radiant power transmitted by the sample. (Sub-units milliabsorbance : mA)

$Loy\ 10\ I/I_o = A$

Absorption ; percentage:

100 (I - Io)/Io (htis definition is not officially recognized in spectrometry). It is a pure number expressing,the ratio of incident light which is absorbed.

Accuracy:

Concept expressing the degree of difference between a measured value and the "True Value". The true value is not known but may be estimated.

Let Xo be the mean value of n measurments, and X the estimate of the true value, accuracy is generally expressed as :

100 (X - Xo)/X

Note: Accuracy of a method is independant from precision, sensitivity, random errors but depends on bias, systematic error.

Amplifier read. out noise:

Noise due to electronic processing of the signal and any errors in the readout device (LIDDELL). This noise is generally negligible.

Background correction:

Device for correction of flame molecular absorption at low wavelength (below 240 nm) necessary for Sb, Bi, Cd, Cd, Co and especially Zn ; Pb .

Bandpass (spectral) :

Part of the spectrum reaching the photomultiplier after leaving the exit slit of the monochromator (usually 0.2 nm to 2 nm for most instruments).

Spectral bandpass is a characteristic of a monochromator the spectral bandpass changes according to setting of the exit slit of the monochromator depending on the geometry of the optical system.

(Also called spectral bandwidth or improperly spectral slit width).

Curve corrector:

Microprocessor insuring a constant slope of signal readout. Compensation of the loss of linearity is purely artificial and does not suppress the physical occurence of the loss of sensitivity associated with loss of linearity.

Dark current noise:

Due to emission of electrons from the photocathode without the arrival of a photon, (LIDDELL).

Detection limit:

Minimum concentration of the measured element that can be detected with 95% probability. In practice it is the concentration for which the absorbance has a value equal to twice the standard deviation of a series of at least 10 consecutives measurements of a blank.

Dissociation energy of an oxyde:

The enthalpy energy of formation of oxydes expressed as Kilocal. x moles^{-1}at 25°from the solid state. The higher the absolute value of enthalpy, the more difficult it will be to dissociate the oxyde. Enthalpy of formation of oxydes of copper, zinc, manganese is low compared to Aluminium or lanthanum oxyde.

Energy level:

Characteristic of an atom being in any state having a higher energy than ground state level. Energy levels are identified by a number of characteristics:

a- Level above ground state: electron-volt (ex: 2,932 Ca...)
b- Total angular momentum of electrons: J
c- The level parity due to angular momeutum of optical electron ; parity is even $^{(+)}$or odd. (-).
d- Compling mode of electron (dipolar etc...)
Energy levels are expressed in wave number (cm^{-1}).

Flame transmission noise:

Noise associated with fluctuations in transmission due to flame flicker. This noise is more important at low wavelength.

Geometrical slit width:

Geometric width of the exit slit of the monochromator, controlling the spectral bandpass reacting the monochromator (from 0.02 to 1 m/m usually).

Interferences:

- Modification of the absorbance of the element to be measured. Chemical interf.: interference due to formation of an element not easily dissociated into free atoms.
- Ionic interf.: interferences due to the loss of ground state atoms, some of them being ionzed (The reverse being possible).
- Spectral int.: interferences due to the overlapping of the measured absorption line by an extraneous line or band (Mariee).

Note: Interferences are different from matrix effects although they are matrix - dependant.

Internal standard:

Technique diminishing the effet of matrix and nebulization variation by measuring simultaneously the absorbance of two elements in the same flame through a dual, channel system one element is the element to be determined, the other one is called internal standard. Effects of variations are eliminated by measuring the ratios of absorbance of the two elements.

Note: This technique requires the use of a dual channel (two HCl, two photomultipliers ...,two monochromators...).

Ionization potential:

Energy necessary to transform one atomgram of element in ground state, to the first ionic valency in electron - volt (...eV).

The lowest value is 4,16 for Dubidium
The hyhest value is 18,6 for Fluorine

Elements having an ionisation potential inferior to 7,5 ev may be partly ionized at the temperature reached by the flames used in AAS. (ie - K, Na, Ba, Li, La, Sa, Cs, Al, Ca, Cr, Mo, Pb).

Note: 1 eV = 1/27 atomic energy unit = 8565.63
values are listed for each element as Ei.

Lamp flicker noise:

Noise due to fluctuations in the output intensity of the light source (Lidell)/

Mean value:

The sum of a serie of measurements divided by their number.

Noise:

Variation of a signal due to uncontrolled flicker of physical parameters (light - emission - absorption - current ...).

Multi-element lamp:

Hollow cathods lamps suitable for analyting several elements. Use of such lamps necessitate good r.l.d as spectral interference may occur. Linearity range of some elements (transition) may be shortened due to the presence of neghbouring non absorbing lines.

Such lamp exist to (Ca,Mg), (Fe, Co, Cu, Ni, Zn), etc...

Oscillator strength:

Pure number associated to absorbing wavelength, for each element in Einstein emission probability theory. This number called f is higher for strongly absorbing lines.

(ex: Zn f = 1.2 for 213,86 nm and 0.00017 for 307.6 nm, which as a relative sensitivity 1/1000).

Photomutiplier:

Vacuum anode - photocell with multiple cathodes which converts photons into electrical current.

Some types of photomultipliers cover the all range 200-900 nm with a loss in sensitivity near infra - red.

Special photomultiplier for working range 400-800 nm are available.

Photon noise:

(Or photomultiplier shot noise). Noise due to statistical fluctuations in the photocathode current, generated by light from the HCL.

Precision:

The measure of the agreement among test results as measured in terms of the standard deviation or relative standard deviation (or variance).

Note: Precision is independant from accuracy but mathematically defined only when the parameter measured is normally distributed around its mean value (Gauss' distribution).

Reciprocal linear dispersion:

Ratio of spectral bandpass to geometrical slit width (expressed in nm/mm). The smallest is r.l.d, the better is the resolution for a given energy falling into the photomultiplier, or in other words, the higher is the energy reaching the photomultiplier for a given spectral bandpass.
r.l.d is the most important characteristic of a monochromator. Actually values as low as 1.5 nm/mm are possible, though the average of the best values is about 2,2 nm/mm.

Relative sensitivity of secondary line:

Ratio of the sensitivy of the most sensitive line to that of a secondary line, for an aqueous solution and optimum conditions.

Repeatability:

Standard deviation or (r.s.d) of a serie of test results carried out in the same laboratory with the same operator and the same apparatus.

Reproducibility:

Standard deviation (or r.s.d) of a group of test results carried out at several laboratories by different operators using the same method but different apparatus.

Resolution (of a monochromator):

The smallest spectral bandpass achieved by a monochromator. (Actually the best resolution being 0.02 nm with an average of 0.2 nm for most instruments). The smaller the resolution, the better the sensitivity, and the wider the range of linearity (as a rough tumb's rule).

Resonance line:

Line emitted from resonance level to ground state level. The resonance level being the level of lowest energy of an atom which can interact with the ground state by an electric dipolar transition. (The variation of J value being not more than unity).

Rich - lean:

Refers to the relative quantity of fluel in flame stoechiometry.

Sensitivity:

The general meaning is the ratio of the increment of the effect to the corresponding increment in the cause, in AAS measurement, the ratio between the measured quantity (in absorbance) to the corresponding increment in concentration (any unit, usually ppm).

The so-called "sensitivity" of AAS spectrophotometers for a given element is the characteristic concentration giving an absorbance of 44 mA (or 1 percent - absorption or 99 percent transmission).

Standard addition:

Technique which compensates for physical, and some chemical interferences of the sample matrix by the addition of a known quantity of standard to the sample. The absorbance difference between the spiked and inspiked sample gives the slope of the calibration curve. (ILL tech. bulletin 42208 - 01).

Note: Unless the "internal standard" method, this technique may be used with any spectrometer.

Standard deviation (s):

The square root of the variance, the relative standard deviation is 100 s/m , m being the mean value.
(r.s.d was formerly called vatiation coefficient).

Stoechiometry of flame:

Composition of flame insuring neutral reaction as far as reduction or oxydation is concerned. This term means a wider range than the chemical stoechiometric reaction occuring between fuel and oxydant.

Variance:

The sum of square of deviations from the mean value divided by the degree of freedom of the population.

VI. ANALYSIS OF Fe, Mn, Co, Cu, Zn by AAS

SELECTED BIBLIOGRAPHY

Analysis of Fe, Mn , Co, Cu, Zn
By Atomic Absorption Spectrometry

(Experimental Conditions and Selected Bibliography)

- Part VI -

- Selected Bibliography -

Most of the papers treating the subject of Micro-nutient analysis by AAS include several elements together. We shall only consider, in this short bibliography, some of the transition elements, i.e. : Fe, Mn , Co, Cu, Zn.

We have chosen copper as main key word, therefore when several elements, including copper, are studied in one paper, reference has to be found under "copper" heading.

Copper is one of the elements most frequently determined by Atomic Absorption and is used as a standard to calibrate instruments; Copper is furthermore quantitatively extracted by a number of organic solvents and its analysis may be used to check the efficiency of a solvent - extraction procedure.

Under the title " transition elements " one would find more general studies, including more than six elements. Such studies, are generally less specific for each element but may be very useful to evaluate a given extraction procedure.

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- TERASHIMA - (On interf. by silicon, aluminium, manganese) (op. cit)

IV. Manganese

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Poch 1, 222, 1975

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SSSAJ 40, 282, 1976

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SSSAP 39, 782, 1975

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ANA 3, 345, 1975

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AAN 4, 289, 1975

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Workshop soil, water, plant analyses,
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93 - MINEAR - "Analytical techniques for measuring and monotoring trace metals."
JAWW. 67, 9, 1975

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Serie No. 73 - page 230

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hydroxyquinaldine:

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diethyl-dithiocarbonate:

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S	1535 R	Copper in soil (1969-1971) 81/ref.
S	676 R	Manganese in soil (1956-1963) 91/ref.
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SA	1898	Extraction methods in soil analysis (1973-1976) 144 ref.
SB	1839	Leaf analysis as a guide to plant nutrient status - (1960-1975) 597 ref.
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J.M

List of Abreviations

AAN : Atomic Absorption Newsletters
AAZ : Annals of Arid Zones
AC : Analytical Chemistry
ACA : Analytical Chemica Acta
AFEG : Annales de la Falsification et de l'Expertise Chimiques
AG : Agrochimia
AGRO : Annales Agronomiques
AJ : Agronomy Journal
AJAR : Australian Journal of Agricultural Research
AJSR : Australian Journal of Soil Research
AJSS : Australian Journal of Soil Science
AL : Analytical Letters
AML : American Laboratory
ANA : Analusis
ANEA : Annales de Edafologia Y Agrobiologia
AN(L) : Analyst
ANUT : Annales de la Nutrition et de l'Alimentation
ATRO : Agronomie Tropical
AS : Applied Spectroscopy

BAFES : Bulletin de l'Association Francaise d'Etude du Sol
BSCB : Bulletin de la Societe Chimique Belge

CAB : Commonwealth Agricultural Bureau
CAPS : Current Advances in Soil Sciences
CC : Cereal Chemistry
CCM : Clay and Clay Minerals
CEB : Cebedeau
CFT : Coton et Fibres Tropicales
CGEO : Chemical Geology
CI : Chemistry and Industry
CIEN : Cientifica
CINST : Chemical Instrumentation
CJS : Canadian Journal of Spectroscopy
CJSS : Canadian Journal of Soil Science
CM : Clay Mineral (Formerly Clay Mineral Bulletin)
CSIRO : Commonwealth Scientific and Indees Des Organisations
CSLT : Canadian Society of Laboratory Technologists
CSR : Chemical Society (London) Review
CSSPA : Communication in Soil Science and Plant Analysis

EA : Electro Chimica Acta
EL : Environmental Letters
ELAC : Electroanalytica Acta
EJSS : Egyptian Journal of Soil Science
EP : Environmental Pollution
ESC : Environment Science and Technology

FZAC : Fresenius Zeitschrift Fuer Analytische Chemic

GEODR: Geoderma

HOLZ : Holzforshung

IAN : Instrument and Apparatus News
ICE : Indian Chemical Engeneer
IJAC : Indian Journal of Applied Chemistry
IJAR : Indian Journal of Agricultural Research

JAOAC: Association of Official Analytical Chemists Journal
JAE : Journal of Applied Ecology
JAFC : Journal of Agriculture and Food Chemistry
JARE : Journal of Arid Environment
JAS : Journal of Agricultural Science
JAWA : Journal of American Water Works Association

JFS : Journal of Food Science
JRC : Journal of Radioanalytical Chemistry
JSFA : Journal of Science of Food and Agriculture
JSS : Journal of Soil Science (Oxford)

LF : Landwirtschaftliche Forschung
LP : Laboratorium - PRAXIS -

MA : Mikrochimia Acta
MAJ : Madras Agricultural Journal
MC : Marine Chemistry
MPB : Marine Pollution Bulletin

NAT : Nature
NZJA : New Zealand Journal of Agriculture
NZJAR: New Zealand J. of Agricultural Research
NZJS : New Zealand Journal of Science

ORSTOM:Office de la Recherche Scientifique et Technique Outre-Mer

POCH : Pochvedenie
PS : Plant and Soil

SA : Spectrochimica Acta
SACP : Society for Analytical Chemistry Proceedings
SAF : Sols Africains
SAJSS: South africa Journal of Soil Science
SF : Soil and Fertilizers
SLF : Schweizerische Landwirtschaftliche Forschung

SS : Soil Science
SSPL : Soil Science and Plant Nutrition
SSS :Soviet Soil Science
SSSAP: Soil Science Society of America Proceedings

TAL : Talanta
TAG : Tropical Agriculture
TE : La Technique de l'Eau
TEC : Technology

XRS : X-Ray Spectrometry
WASP : Water, Air, Soil Pollution
WR : Water Research
WRS : Water Resources Research

I.M