ATOMIC ABSORPTION SPECTROSCOPY

Instrumental Conditions

DAMASCUS - 1978

THE ARAB CENTER
FOR THE STUDIES OF ARID ZONES AND DRY LANDS
(A C S A D)

THE ARAB CENTER

For The Studies of Arid Zones & Dry Lands

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— ATOMIC ABSORPTION SPECTROSCOPY —

INSTRUMENTAL CONDITIONS

Damascus 1978

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- A.C.S.A.D. -

- TECHNICAL NOTES - N° 1

- Atomic Absorption and Emission in Flame.

INTRODUCTION

This booklet intends to facilitate the choice of experimental para-
meters for beginners in Atomic.- Absorption - It includes main elements
usually determined in soil and water samples.

Optimization of experimental conditions may serve either the pur-
pose of getting the best precision or the best sensitivity. These qua-
lities are somewhat contradictory. So are most the parameters on which
depend the final analytical result. This is why an average setting is
usually given in operation booklets of instrument makers. The following
informations include average and optimum adjustments.

It is assumed, that experimental conditions leading to accurate
results are realised. These conditions may be summarized as follow:

a. Viscosity and acidity (percent of acid in water) of unknown and
   standard solutions are identical. Optimum in percentage of acid is
   around 1 to 2%. Above 5% viscosity an anion effect become noti-
   ceable.

b. The solution of soil or plant should be preferably done in HCl,
   $HClO_4$ or HNO_3. Others minerals acids as H_2SO_4 or H_3PO_4 produce
   a considerable loss in sensitivity.

c. It is also assumed that the matrix of the sample is known so that
   chemical interferences and effects, due to ionization and matrix
   can be overcome.

d. The solution is free from solid particles which show a non-specific absorption and cause signal instability.

DEFINITIONS

a) we used notation p.p.m (part per million) for micro-gram/milliliter, for an easier typing, despite the fact that they usually represent slightly different numbers.

We have used:

$\underline{m}$: maximum concentration expressed in ppm, for which the calibration curve is a straight line.

$\underline{s}$: sensitivity: concentration (expressed as ppm) giving 1% Absorption, or 4,4 milliabsorbance; sensitivities are average of datas given by several makers and represent usually the best conditions obtainable in aqueous solvent.

$\underline{l}$: detection limit: minimum concentration (expressed as ppm) for which ten successive measurments give an average absorption at least equal to two times average ground noise.

$\underline{p}$: precision: if n measurments are made on a solution having a concentration around m/2 and if v is variance of this n measurments :
then: $p = 100 \ v/M$ (n must be higher than 10).
M = mean value of these n measurements.

How to use given indications:

a. Experimental conditions are given in chronological order of operation.
- Preparation of standard solutions.
- Lamp current (Approx.).
- flame stoechiometry.
- burner eight.

- Main Line/secondary line with associated slit width.
- Interferences and their suppression.
- Internal standard.
- Depressing and Enhancing solvents.

- no indication has been given concerning photomultiplier voltage setting; it has to be adjusted, after the choice of optimum band pass (slit-width) so that saturation of P.M is not reached.

- sensitivities of secondary lines are given relatively to sensitivity of main line taken as unity.

- Stoechiometry is expressed as ratio of gaz flows (fuel/oxidant). Some instruments indicate pressures, making a conversion necessary.

- no data is given for aspiration rate, as departing from the optimum of each nebulizers will usually increase background noise while decreasing sensitivity.

Preparation of interference suppressors:

- Strontium chloride:
- weight 152,5 g $SrCl_2$, $6H_2O$, dissolve in on lirer of bi-distilled water final solution is 5% Sr (w/w).

- Lanthanum chloride:
- Ca and Mg stock solutions and samples should be done in a 0.5% La aq. solution. It is therefore useful to have a large quantity of 5% La and 0.5% stock sol. for making dilutions when necessary.

- weight 5,85 gr of La_2O_3 slowly dissolved in minimum 50% HCl (violent reaction) adjust to 1 l with deionized water. Solution is 5% La (w/w). (using the chloride directly is just much more expensive at equivalent purity).

- ALUMINIUM -

- Al -

Al n = 13 M = 26,981 $f(Al_2O_3/Al_2)$ = 1,8895 1/f = 0.5292

MODE:

Emission has a better sensitivity than absorption.

ABSORPTION:

1. ### Stock Solutions:

    a. 1,000 g Al 99,99% dissolved int. 100 ml conc. HCl after having added 1 drop of Hg. The solution adjusted to one liter is 1000 ppm.

    b. 0.5294 g/l of Al gives: a 1000 ppm sol.in Al_2O_3.

    c. organo metallic compound: Aluminium. cyclohexane butyrate or Aluminium 2 ethylhexanoate.

2. ### Lamp:

    Sensitivity decrease as current increase. (best sens.for 6.8 mA and best precision for 8 - 10 mA).

3. ### Flame:

    The only usable flame is C_2H_2/N_2O stoechiometric.

4. ### Burner Height:

    5 m/m. (given as height of light path above the burner).

5. ### Main Line:

    309,27 + 309,28 nm (band pass 1 nm).
    l = 0.05   m = 30 - 60
    s = 0.6   p = 0.3%

6. **Secondary Lines:**

line		band pass
396,15	0.8	0.5 nm
308,22	0.7	0.5 nm
394,4	0.5	0.5 nm
237,34	0.25	0.5 nm
237,84	0.16	0.5 nm
257,54	0.12	0.5 nm
256,80	0.08	0.5 nm

7. **Interferences:**

   - No interferences of Ca - Zn - Pb - Mg - P
   - Slight int. from Fe - Cl. (Adjust Cl conc. of standard and unknown if HCl is used for sample preparation).

8. **Correction of Interferences:**

   - **Fe** add the same quantity of Fe to samples and standards to correct enhancement due to Fe.
   - **Al** is slighty ionised in hot C_2H_2/N_2O flame. An ionization buffer (K, Cs, Sr, 1% as chloride) is added, and chloride concentration needs to be adjusted.

9. **Enhancing solvent:**

   - n-butanol, isopropanol, Ethanol.

10. **Depressing solvent:**

   - Hydrochloric Acid, chloride rich solutions.

EMISSION

   - Flame: C_2H_2/N_2O stoech./rich (red feather 20/30 m/m).
   - main line:396,15 nm (1 = 0.01 s = 0.5).
   - Secondary Lines: 394,4 nm and 309,3 nm.

INTERFERENCES:

If solution is rich in Ca, emitting at 396,80 nm, the 396,15 nm line is to be avoided.

CONCENTRATIONS:

- Soils: from 2 to 30% in Al_2O_3

- Plants: from 2 to 5000 ppm

- Waters: up to 5 ppm.

REFERENCES:

- GUEST. Mc Pherson. The use of flame procedures in metalurgical analysis. Part II. Determination of Al in sulphide and silicate material, ores and slags.
  A.C.A. 78, 299, 1975.
- C.A.B.: Chemical det. of Al in soil and plant material Annotated Bibliography (1967 to 1974) N- 1674 Com. Agric. Bureau, Slough, ENGLAND.

- CALCIUM -

Ca   n = 20   M = 40,0   f(CaO/Ca) = 1,399   1/f = 0.714

1 eq/1 = 20,04 ppm   f(CaCO$_3$/Ca) = 2,495   1/f = 0.401

1 ppm = 0.05 meq/1

MODE

emission is more stable, more sensitive and less subject to chemical interf. than absorption.

ABSORPTION

Stock Solutions

a 1000 ppm sol of Ca (i.e 50 meq/1) is obtained from:

a.   2,7693 gr/1 CaCl$_2$

b.   2,4973 gr/1 CaCO$_3$ dissolved in minimum 10% HCl, complete to have final concentration 1,25% in HCl.

organometallic compound: calcium - 2 - ethylhexanoate.

Lamp: sensitivity decreases as current increases if max. lamp current is 10 uA, best sensitivity is for 6 uA and best precision for 9 uA.

Flame: C$_2$H$_2$/air (1/3.5 - 4.5) stoeck. or lean but with maximum gas flow; this flame is non ionizing but subject to many interferences. C$_2$H$_2$/N$_2$O (1/1,5 - 1,8) stoeck. less sensitive but free from main interferences. Needs an ionization buffer (0.1% KCl, KNO$_3$, Cs...) to reduce Ca^{++} concentration.

Burner height:

between 5 and 10 m/m for C$_2$H$_2$/air flame.

<u>Main Line:</u> 422,7 nm (band pass 0,4 - 1,0 nm)

    for C_2H_2/air   s = 0.05   m = 10

    for C_2H_2/N_2O s = 0.02   m = 5 (Conc. given in ppm).

<u>Secondary Lines:</u>

239,86 relative sensit. 0.005 (band pass 0.15 nm).
allow to work in the range of 200 - 1000 ppm.(poor signal to noise ratio)

<u>Interferences:</u>

a.   Important interf. from PO_4, SO_4, Al, Si, NO_3. corrected by a 1% La addition in standard and unknown if not too much Mg is present.

b.   if concentration of Mg is important, standard and unknown must be Mg saturated(ratio Mg/Ca about 100) care must be taken for samples containing phosphate, gypsum, dolomite.

c.   no interference of K, NH_4, OH, Cl, CO_3.

d.   all mineral acids cause a slight decrease in Ca concentration.

e.   in solution rich in Si & Al it is necessary to use C_2H_2/N_2O flame and add Sr to both standard and unknown.

<u>EMISSION</u>

- flame:
  - C_2H_2/N_2O lean (5 m/m red feather).
  - C_2H_2/air with decreased sensitivity.

- main line: 422,67
  - l = 0.0003   m = 5 to 10
  - s = 0.003

A narrow bandpass is recommended to avoid disturbance due to the nearby strong emission of CN at 421 nm.

CONCENTRATIONS

- Plants   : 0,1 to 10% (105° dry weight basis)
- Water   :-drinkable: less than 150 ppm

    -from Limestone areas 50 to 150 ppm

    -from gypseous - rich areas: 100 to 500 ppm.

-Soils, Rocks-from 0 to almost 40% Ca (equiv. to 100% $CaCO_3$).

REFERENCES:

-    WARD, BIECHLER: "Rapid, direct determination of Ca in natural waters by A.A.S.

    A.A. Newsletters 14, 29, 1975.

-    MAHJOURY: Clay Mineralogy, physical and chemical properties of some soils in arid regions of Iran.

    S.S.S.A. proceedings 39, 1157, 1975.

-    C.A.B.: Chemic. det. of Ca and Mg in soil and plant material. Annotated Bibliography N- 1675 - Commonwealth Agricultural Bureau, 1975.

- COBALT -

Co n = 27 M = 58,9332 f(CaO/CO = 1,2714) 1/f = 0.7864

MODE

Absorption is more sensitive than emission.

ABSORPTION

Stock Solutions 1000 ppm of Ca

1. 1,000 gr of metal dissolved in minimum conc. HCl.
2. 4,038 gr of $CoCl_2$, $6H_2O$ or 4,9379 gr of $Co(NO_3)_2$ in one liter. Since these salts are extremely hygroscopics, checktitration by complexometry is necessary. (see appendix).
3. organometallic compound: Cobalt cyclohexanebutyrate.

Lamp: sensitivity decrease: slightly as lamp current inc. a good compromise is obtained at 50% of max. lamp current.

Flame:

C_2H_2/Air stoech. the most stable.

C_2H_2/Air reducing the most sensit.

C_3H_8/Air reducing

C_2H_2/N_2O gives better results than other combinations.

Main Line:

240,73 nm (band pass maximum 0.3 nm)

s = 0.1 m = 5

Secondary Lines:

242,49 nm r.s = 0.8 range 2 to 50 ppm
241,46 nm   0.5
252,14 nm   0.3

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243,58 nm    r.s = 0.3
304,40 nm          0.08   band pass 0.5 nm
352,59 nm          0.06   range 100 to 2000 ppm
346,58 nm          0.03   band pass 0.15 nm
341,26 nm          0.03   band pass 0.15 nm
347,40 nm          0.02   band pass 0.15 nm
301,76 nm          0.01
391,0  nm          0.005  band pass 0.5 nm
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Interference

- Non specific absorption around the main line (240 nm) correc-
  ted either by Deuterium - continuous emitting Lamp background
  correction or by measuring non specific absorbance at 238,8
  nm and "substracting" it from the final result (or adding if
  dealing with absorbance readings)

- No noticeable interference in diluted solutions.

- Interference of Fe, Ni, Cr if present in high amounts (1500
  ppm Ni produce a 50% decrease of the signal).

Enhancing Solvants:

- 70% isopropanol in water is a solvant doubling sensitivity
  (for 240,73 nm line).

Particularities:

- Precision at low concentration is very poor and depends
  strongly on flame conditions which are to be adjusted with
  utmost care.

EMISSION:

- Main Line: 345,35 nm

- Flame : C_3H_8/Air: best flame

  C_2H_2/N_2O: (red feather 2 m/m) (caution : to much lean a flame is likely to explode inside the burner).

CONCENTRATION

Soils

- 1 to 40 ppm (average around 5 ppm).
- ultrobasic (serpentines...) 0 to 2%

Plants

- 0.01 to 1 ppm in usual soils (wide range of concentration in Co rich soils, in endemic species).

REFERENCES:

- WARREN - CARTER: Det. of trace amounts of Cu, V, Cr, Ni, Co, Ba in silicate rocks by flame A.A.S. Can.J. of Spectroscopy 20,1,1975.
- SAPEK: A.A.S. Det. of Pb, Ni,Co in soil extracts Chem. Analysis (WARSAW) 19, 687, 1974.
- SINHA-BANERJEE. Interf. in estimation of trace amounts of Co, Cu and Zn in soils by A.A.S. Technology (SINDRY - INDIA) 11, 263, 1974.
- HOCQUELLET. Det. of Co in animal feeding stuffs by flame and flameless A.A.S.
  Annales. Falsif. Expert Chimiste. 67, 495, 1974.
- HARA, SONDRA, IWAI. Growth response of cabbage plants to transition elements under water culture conditions. Part II. Co, Cu, Zn, Mo.
  S.S. Plant. Nut. 22, 317, 1976.

- Cu -

n = 59   M = 63,646   f(CuO/Cu) = 1,251   1/f = 0.798

MODE:

Absorption is more sensitive.

Absorption:

- Stock Solutions: 1000 ppm Cu:

    1.   1,000 gr of metallic Cu dissolved in 3 ml HNO_3 conc. (cold)
    2.   3,929 gr $CuSO_4$, $5H_2O/1$ H_2O.
    3.   3,798 gr $Cu(NO_3)_2$, $3H_2O/1$ H_2O. If this option is chooser, Cu concentration has to be checked by complexometry (see appendix).

    Lamp current:

    If max. lamp current is 5 - 7 mA, optimum is 4 maximum sensitivity is 3 and max. precision 4 - 5 mA.

    Flame:

    C_2H_2/Air stoech. of Lean.

    C_3H_8/Air gives a better sensitivity.

    Burner height:

    11 m/m for C_2H_2/Air stoech. flame.

    Main Line: 324,75 nm

    1 = 0.006   s = 0.06   m = 4 to 6
    (1 ppm produce around 100 milliabs.).

Secondary Lines:

line	relative sens.		band pass (nm)
327,4 nm	r.s	1/2	0.5
217,89		1/5	0.3
218,2		1/5	0.3
216,51		1/6	0.3
222,5		1/10 1/20	0.15
249,22		1/100	0.5
244,16		1/300	1

Interferences:

- large excess of transition elements give a depressed reading, especially for Zn.

- Cu is one of the elements giving the most easy-to-read results. (if no computored - integration is available).
- virtually no other interf. by other elements in C_2H_2/air flame.

EMISSION:

Line: 327,40 nm : max. sensitivity

324,70 nm : less sens.

both line have to be used in conjonction with the minimum band pass (and maximum photo multiplication) a lean C_2H_2/N_2O flame is more sensitive that C_2H_2/Air stoech.

Concentration:

Soils : 2 - 200 ppm

plants: 1 - 25 ppm

Water : drinking water : max. 1 ppm

irrigation water: max. 0.5 ppm

- Fe -

Fe   n = 56   M = 55,847 $f(Fe_2O_3/Fe_2)$ = 1,429   1/f = 0.699

$f(FeO/Fe)$ = 1,286   1/f = 0.7773

ABSORPTION:

- **Stock solution** (1000 ppm Fe)

- 1,000 gr pure Fe in 5 ml HCl conc. (add few drops of HNO_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 $FeCl_3$, $6H_2O$, control Fe concentration by complexometry.

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

Lamp current:

max. precision is near max current max. sensitivity is 70% of max. current.

Flame:

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

Main Line: 248,33 nm

1 = 0.01   s = 0.1   m = 5.10

Other Lines:

Fe has many absorbing lines. Among them:

248,81	r.s	1/2
252,21	r.s	1/2
271,98	r.s	1/3 (relatively large band pass poss.)
302,06	r.s	1/4

252,74	r.s 1/5
371,99	1/8 (band pass 0.3 nm, very stable meas.)
269,69	1/9
385,99	1/12 (band pass 0.3 nm - doublet).
344,06	1/100
392,03	1/250 (band pass 0.3 nm).

Interferences:

- Especially from Si and PO_4. This chemical interference is depending on instrument settings.

- With C_2H_2/Air oxydant (very Lean), Fe interf. are decreased, together with sensitivity.

- Interference of Si may be overcome by using a 0.2% $CaCl_2$ sol as int. standard (see annex), or by using the hotter C_2H_2/N_2O flame.

- No Interference from
  - 3000 ppm K, Ca
  - 1000 ppm Na, Mg, SO_4, Cl, transit. metals.

- Background correction 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).

- **Concentration:**

  Water : surface water alcaline surface: less than 1 ppm.
  under ground water: 1 - 3 ppm.
  drinking: less than 0.1 to 0.2 depending on local regulations.

REFERENCES FOR TRANSITION ELEMENTS - (see also Co page 13.)

- PINTA: Plant Standards for the analysis of leaves.
  ANALUSIS, 3, 345, 1975.
- WALLINGFORD & al: Effects of beef feedlot manure and lagoon water
  on Fe, Zn, Mn, Cu content in corn and DPTA soil extracts.
  SSSAP 39, 482, 1975.
- KORKISCH, SORIO. Appl. of ion exchange methods for the det. of
  trace elements in natural waters. Part VII: Cu
  Talanta 22, 289, 1975.
- SANZOLONE - CHAO. A.A.S det. of Cu, Zn, Pb in geol. materials.
  A.C.A 86, 277, 1976.
- WARD - BROOKS - REEVES. Det. of Cu, Cd, Pb, Zn in soils, stream
  sediments, waters, and nat. vegetation around Tui Mine.
  N. acaland J of Science 19, 81, 1976.
- C.A.B. annotated bibliography on chemical det. in soil and plant
  N- 1679 for copper, N- 1681 for Fe, Mn. Commonwealth Agricultural
  Bureau, Slough, ENGLAND.

- POTASSIUM -

$n = 19$ $N = 39,102$ $f(K_2O/K_2) = 1,204$ $1/f = 0.830$

1 millieq = 39,102 milligram.

MODE:

The best advantage of emission over absorption is to ellow to work at 404,4 nm and give a very low sensitivity, without supressing interferences.

ABSORPTION:

Stock solutions: 1000 ppm of K: (25,62 meq/l.).

- 1,907 gr KCl, dry 105° dissolve in 1 l.
- 2,586 gr KNO_3, dry 105° dissolve in 1 l.
- organo-metallic - Cyclohexanebutyrate of K.

Lamp:

max. precision 80% max. current.
max. sensitivity 50% max. current.

Flame:

The best flames are in the order:

C_4H_{10}/Air: cylindrical burner, no interferences.

C_3H_8 /Air: few interf.

C_2H_2 /Air: (Lean) important interf. of sodium.

burner height:

Critical for reducing interference of sodium. Less than 1 m/m with C_2H_2/air flame.

<u>Main Line</u>: 766,5 nm (resonnance Line).

$$l = 0.002 \quad s = 0.05 \quad m = 2 \text{ ppm} \quad (\text{data for } C_4H_{10}/\text{air flame}).$$

<u>Secondary Lines</u>:

769,9	r.s 1/2 (band pass 1 nm - resonnance Line)
404,72/404,41	r.s 1/200 (band pass 0.4 nm - doublet).

<u>Interference</u>:

As for all **alcaline** metals, ionization causes a depression of the response. Thus, easily ionizable elements, Na, Rb, Cs, Li enrich the flame in electrons reduce the number of K in the sample and gives a final overestimated result. A ionization buffer 0.1% Cs of Sr[*] supress this effect (it has to be added to both standard and samples). A decrease in flame temperature is also of benefit.

<u>Enhancing solvent</u>:

- Butanol 4% (in water).

<u>Particularity</u>:

Potassium emits and absorbs in red-band of visible wavelengths. It may be necessary to change photomultiplier to keep on with max. sensitivity.

<u>EMISSION</u>:

<u>Flame</u> : C_2H_2/Air: blue flame (oxydant).

C_3H_8/Air: blue flame (oxydant).

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[*] Sr cannot be used with sulfate containing solution, because of strontium sulfate precipitation.

Burner height:

    from 10 to 25 m/m depending on burner geometry.

Concentration:

    Soils : 0 to 5% K_2O.

    Plants : 0.2 to 10%.

    Waters : surface:5 - 15 ppm.

               ground : usually less than 20 ppm. may reach higher

                    conc. occasionally.

REFERENCES:

    (see Ca and Na also)

- NEUNER & al: Automated flame photometric det. of K_2O in fertili-
zers.

    J. Asso. off. Anal. Chemists 58, 923, 1975.

- Mg -

n = 12   A = 24,305   f(Mg/MgO) = 1,658   1/f = 0.603

1 meq = 12.15 mg

MODE:

ABSORPTION:

Stock solution: 1000 ppm (82,4 meq/l.).

- 1,000 gr of Mg ribbon diss. in 7 ml conc. HCl and adj. to 1 l.
- 3,916 gr $MgCl_2$, $6H_2O/1l$ H_2O.
- organo-metallic compound: many organo-magnesians.

Lamp current:

- Max. precision obtained for max. lamp current.
- Max. sensitivity 50% max. Lamp current.

Flame:

- C_2H_2/air reducing (rich - yellow).
- C_2H_2/N_2O (1/1:25) stoeck.

Burner height:

8 to 10 m/m.

Main Line: 285,21 (band pass 0.1 nm).

1 = 0.002   s = 0.05   m = 0.4

(0.1 ppm gives, 100 milliabsor bance if correct adj. are made).

Secondary Line:

202,58	r.s	1/25 (band pass 0.8 nm)
279,58	r.s	1/100 (ionic Line)
280,27		(ionic line)

ionic line could be used if much Mg is present in a medium free of other easily ionizable elements.

Interference:

a) Aluminium, phosphate, chloride, Sulphur, Si, depress the response in the C_2H_2/air flame. This effect is reduced by making solution in 1% (w/w) Lanthanum, or Strontium.

b) enhancing effect of acetic ion[*] and alcaline metals. Effect reduced by using an ionization buffer (KCl 0.1% w/w)

c) Varying interferences of Cu, Ti, Fe, Al. All interferences are strongly dependant on size of droplets reaching the flame and can be almost supreésed in laminar flow.(except for Al).

EMISSION:

Flame:

C_2H_2/N_2O Lean. wave Length 285,21 nm. No advantage over absorption.

Concentrations:

- Water:
  - surface (on acid soils or rocks) 0 - 5 ppm
      (on limestone - dolomite) 10 - 50 ppm
  - wells up to 4000 ppm.

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[*] Particular attention is to be paid to exchangeable Mg due to high concentration of acetate in many methods.

- Mn -

Mn + n = 12   A = 54,938 $f(MnO/Mn)$ = 1,2912 $1/f$ = 0,744
                             $f(Mn_2O_3/Mn)$ = 1,4360 $1/f$ = 0,6960

MODE:

ABSORPTION:

Stock solutions: 1000 ppm Mn.

- 3,607 gr $MnCl_2/l$ or 3,076 gr/l $MnSO_4$, 4 H_2O in water.

- 1,000 gr metallic Mn in minimum conc. HCl.

- Organometallic: Mn - cyclohexanebutyrate.

Lamp:

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

Flame:

C_2H_2/air: reducing best sensitivity.

C_2H_2/air: oxydizing best precision.

C_3H_8/air: best stability (good sensitivity).

C_2H_2/N_2O: Lean, 5 m/m red feather. Suitable for 403,08 nm.
              (burner height: 10 m/m).

Burner height:

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

Main Line:

- 279,48 nm minimum available band pass (279,83 and 280,11 peaks must be separated from 279,48).

Secondary Lines:

| 403,08 | r.s | 1/20 (wide band pass possible). |
| 321,70 | r.s | 1/2000 |

Interferences:

- Si even in low concentrations. (correction by addition of 50 to 2000 ppm $CoCl_2$ to standard and sol).

- Phosphates, perchlorates, transition metals (Fe in excess of 25 ppm), in reducing flames.

- No interference of 1000 ppm from Na, K, Ca, Mg. If concentration in these metals.

Concentration:

Sol : 0 - 1% en MnO.
Plant : 5 - 5000 ppm.
Water : less than 0.5 ppm. (surface).
less than 0.1 ppm. (drinking water).

EMISSION:

403,08 nm using a lean C_2H_2/N_2O flame

REFERENCES: (see also transition elements)

- SIMAN - CRADOCK - HUDSON - Development of Mn toxicity in pasture legumes under extreme climatic conditions P.S 41, 129, 1974.

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- Na -

Na   n = 11   A = 22,9898 $f(Na_2O/Na)$ = 1,3479 $1/f$ = 0.7418

1 millieq = 23 mgr   1 ppm = 0.0434 meq/l.

MODE:

ABSORPTION: for 1000 ppm Na : (i.e 43,5 meq/l).

- 2,5420 gr/l NaCl (from 120^OC dried NaCl)
  for 20 meq/l Na.

- 1,1714 gr/l NaCl.

- Organometallic Na - cyclohexanebutyrate.

Lamp:

Sensitivity doesn't decrease when increasing lamp current.
can be used for best precision.

Flame:

C_3H_8/air max. sensitivity. Effect of ionization of other
alcaline metal is reduced by the low temp. of the flame.

C_2H_2/air: Lean (1/5,5) less sensitive, less stable.

Main Line: 589,0   with narrow band pass)

1 = 0.001   s = 0.005   m = 1 ppm

Secondary Lines:

589,59	r.s 1/2	(resonnance line - needs a narrow band pass).
589,0 + 589,59	r.s 1/1.2	(entire doublet band pass 0.6 nm).
330,2	r.s 1/300	(narrowest possible band pass).
330,3	r.s 1/300	(narrowest possible band pass).
or : 330,2 + 330,3	r.s 1/200	

Interference:
===

- Few interfering elements, except from high concentration of Cl or SO_4 ion. Effect from easily ionizable elements is supressed by 1000 ppm of Ca, Li or K as buffer.

Enhancing solvent:
===

n. butanol 6% (w/v in water).

EMISSION:
===

- flame : C_3H_8/air Lean (minimum burner height).
- Line : 589,0 nm (minimum band pass).

Interferences:
===

Unlike Potassium, there are more interferences in emission mode than in absorption Fe, Co are enhancing, in addition, large quantities of Ca cause an increase of background noise due to emission bands of Ca hydroxydes (from 572 nm to 602 nm peak to peak).

Concentration:
===

- The range of concentration, in natural water, in soils and in plants is very wide as just an idea:

  for soils : from 0.1 to 500 meq/l in saturated extract.

  for plants: from 0.01 to 5%.

- Si -

$n = 14$ $A = 28,086$ $f(SiO_2/Si) = 2,1393$ $1/f = 0.4674$

ABSORPTION:

- **Stock solution:** 1000 ppm Si

  a. 117,86 g/l SiO_2, $12NO_3$, $26H_2O$

  b. 7,552 g/l Na_2SiO_3, $5H_2O$ (diluted in hot water)[*].

  c. **2,1393** gr pf pure silica used with 10 gr de solid NaOH
     dilute residue of fusion in hot water.

  d. organometallic : octaphenyl cyclotetrasi loxane.

  Lamp:

    best sensitivity: 50 - 70% max. current.
    best precision : 80 - 100% max. current.

  Flame:

    Only C_2H_2/N_2O Lean with maximum gas flow (to avoid flash -
    back).

  Burner Height:

    Silicium absorbs in a narrow region above the burner (7 to
    8 m/m.

  Main Line: 251,61 m/m

    $s = 1,5$ $m = 150$

---

[*] Exact concentration is to be verified by standard gravimetric
    analysis.

Secondary Line:

250,69	r.s 1/2,5	252,41	r.s 1/5
251,43	r.s 1/3	221,67	r.s 1/5
252,85	r.s 1/4	221,89	r.s 1/10

Interference:

- HF, H_3BO_3 give a depression of the signal.

- presence of an easily ionizable element gives an enhancement.
  Therefore with excess of Na, K, Mg, Ca, a 0.1% buffer of
  any alcaline chloride should be used.

EMISSION:

Line:

251,61 nm - (narrow band pass) flame N_2O/C_2H_2 stoech.
(15 m/m red feather). Measurment at 7 - 9 m/m.

Concentrations:

Plants: 0.01 to 5%

Water : potability limit: 25 ppm.

REFERENCES

MORRIS - Det. of Si in cured tobacco leaf by A.A.S. Tobacco Science 18, 120, 1974.

- Zn -

Zn   n = 38   A = 65,37   f(ZnO/Zn) = 1,2447   1/f = 0.803

MODE:

ABSORPTION:

Stock solutions: 1000 ppm

a.   1,000 gr Zn dissolved in 3 ml of conc. Hcl
b.   1,245 gr ZnO, few drop of water, dissolved in diluted HCl

Lamp:

-   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).
-   C_3H_8/air: (flame absorbing).

Burner Height:

6 m/m for C_2H_2/air flame.

Main Line:

213,06 nm (minimum band pass to exclude the 213,60 Line of Cu)
s = 0.02 ppm   m = 1 ppm

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

APPENDIX

1. ABREVIATIONS:

AAN   : Atomic Absorption Newsletters. (Ed. Sabina Savin. Perkin-Elmer Corporation, Main Ave, Norwalk CT 06856 U.S.A.)

AAS   : Atomic Absorption Spectroscopy).

A.C.A.: Analytical Chemica Acta. (Elsevier Publ. Co P.O.Box 211 - Amsterdam Netherlands).

AN   : Analusis - Société de Productions documentaires 8c Ave. du 18 Juin 92500 Rueil-Macmaison France.

ANA   : Analyst (Ed. J.8 Atrill 9-10 Savile Road LONDON WIXIAF).

ANCH   : Analytical Chemistry.

AOACJ   : Association of Offic. Anal. Chemists (Ed. Reynolds, P.O.Box 540 Benjamin Franklin Station, Washington D.C 20044).

C.A.B.: Commonwealth Agricultural Bureau. Slough - England.

CJS   : Canadian Journal of Spectroscopy.(Moltiscience Publications Ltd. 1253 Me Gill College. Suite 404 - Montreal 110 - CANADA

NZJS   : New Zealand Journal of Science.(Ed. J.C GREORY, Dep. of Sc. and Indus. Research, Private Bay, Wellington New Zealand.

P.S.   : Plant and Soils. (Ed. M. Nihjoff 9-11 Lange Voorhout Box 269. The Hague, Netherlands.).

SSPN   : Soil Science and Plant Nutrition. Japan Publications Trading Co Ltd. Box 5030 Tokyo - International. Tokyo JAPAN.

SSSAP : Soil Science Soc. of America proceedings. SSSA, 677 St. GEORGE ROAD MADISON Wis. 53711.

TAL   : Talanta: Headington Hill Hall Oxford OX3 OBW ENGLAND.

2. Definitions:Methodology

a. **Accuracy**:

measure the agreement between a measured value: m and the value accepted as "true": mo. for instance: $a = 100 (m - mo)/mo$. the smaller a, the more accurate the measured value m. is.

b. **Precision**:

measure the agreement among tests results as expressed in terms of standard deviation or relative standard deviation if n differents values are obtained by the same operator using the same method on the same sample: if further more:
M is the average of these n values.
S is the standard deviation n values.
precision is: $p = 100 \, S/M$.
the smaller p, the more precise the method concerned is.

c. Repeatability:

measure how much a given method is reliable as far as the conste.ncy of its results is concerned: Several series of tests results are performed on the same sample by the same operator using the same method at different periods of time. (two for instance). If S1 and S2 are the standard deviation,the smaller is the difference (S1 - S2), the more repeatable is the method.

d. Reproductibility:

measured by the standard deviation of a serie of test results given by differents laboratories, using the same method on the same sample.

3. Definitions: Apparatus

a) Intrinsic properties of apparatuses:

- Resolution:

The resolution, given in nm units, is a fixed property of a given monochromator (single or double grating). A usual figure is 0.2 nm (from 0.05 to 0.4 nm). A resolution of 0.2 nm means that two lines distant of 0.2 nm (peak to peack) are folly separated.

- slit width:

measure the amount of light reaching the photomultiplier. One should always choose the widest slit compatible with the selection of only one resonance line.

- reciprocal linear dispersion: (r.l.d)

measure the spectral bandwidth for a geometric slit width of 1 mm. A small linear dispersion (nm/mm) means that a small spectral bandwidth is associated to a wide slit, the result being a high signal to noise ratio. (Double-grating may have a r.l.d of 1 nm/mm in v.v) value of 1.3 to 4 nm/mm are reported by manufactures.

b) display and read-out accessories:

a wide range of display and read-out recording systems is actually available, among the mode of display:
- scale voltmeters: (scale calibrated in % Absorption or Absorbance units).

- Digital voltmeters: connected to a micro-computer allowing:

- discontinuous display (various sequences of time)
- integration over a given period of time
- peak height measurment
- peak surface value
- average.

Among the read-out recording systems.

- in addition to the above mentioned devices, record of results
can be achieved either by a digital printer or a strip-chart
potentiometric recorder. Each system has its pros and cons,
but only a strip-chart recorder provides a complete show of
what-is-going-on during the all process. It is a good prac-
tice to keep in mind how much reach the absorption percenta-
ge during each sample aspiration. Digital voltmeters are
very accurate and versatile but one has to know that when
a result is given in integrated mode (i.e on average, a sur-
face) the fluctuation of the signal doesn't appear. The
some remark is valid for artificial zeroing of the baseline.

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Methods of dissolution of siliceous samples for AAS (Pye unicam 1975.
ENGLAND).

5. <u>CHECK TITRATION OF Co STOEK SOLUTION</u>:

- Stock solution supposeddly 1000 ppm is diluted 10 times. To
  a 20 ml aliquot add: 3 ml of PH 4,3 buffer (ACoNa 105 gr/l in
  Acetic Acid 10%), 5 drops of Alizarin complexone indicator and
  3 drops of xylene cyanol FF. Heat to 80° and titrate with
  $2 \times 10^{-2}M$ EDTA to a green end-point. (change of color is
  from grey to red and to green.

<u>optional method</u>:

To a 20 ml aliquot add 25 ml dist.water, 5 ml of PH 4,5 buffer
(ACoNa 136 gr/l in Acetic Acid 6%), 5 drops of xylenolorange tetra-
sodic salt (0,2% in water) heat to 70-80°C, and titrate to violet-
to-yellow end-point.

6. <u>CHECK TITRATION OF Mn STOEK SOLUTIONS</u>:

- when dissolving metallic Mn in acid, a brown precipitate of
  MnO_2 may be formed. Add 10% sodium hydrosulfite $Na_2S_2O_4$ un-
  till it redissolves.

<u>Titration of Mn (II)</u>:

- Dilute 10 ml of the supposed 1000 ppm stoek solution to 100 ml,
  add 1 gr of ascorbic acid, dissolve. Add 5 drops of solochrome
  black T as indicator 10 ml of buffer PH 10 (70 amonium chloride
  added to 570 ml of conc. amonia sol, diluted to 1 l) titrate imme-
  diately with $2.10^{-2}M$ EDTA to the red to blue end-point, (from T.S
  West, complexome try with EDTA and related agents, BDH publ.).

- Mn (II) is converted to MnO_4^- by amonium persulfate or sodium
  bismutate oxydation. Pink MnO_4^- is titrated back to Mn(II) by
  ferrous salt.

- To 10 ml solution add sufficient nitric acid to have a final
  concentration 2,4 M about add 15 ml silver nitrate 0,1 M and 50 ml
  of ammonium persulfate 10% - Heat to 80° - 100° for 15 min titrate
  by Mohr salt N/10 just to disapearance of the pink color.

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المركز العربي لدراسات المناطق الجافة والأراضي القاحلة

(أكـــــــــاد)

ص.ب ٢٤٤٠ دمشق ـ سورية

برقياً : أكساد ـ دمشق هاتف ١١١٧١٨
١١١٩١٣

أنشىء في نطاق جامعة الدول العربية وباشر عمله بتاريخ
ـ ١٩٧١/٩/٢٥ . له شخصية اعتبارية وميزانية مستقلة .

مركزه ـ مدينة دمشق ـ سورية ، وله أن ينشىء فروعاً
في الدول العربية .

يهدف الى القيام بدراسات اقليمية تتعلق بالمناطق الجافة
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والجوفية والاراضي والبيئة النباتية والثروة الحيوانية بقصد
تحسين استغلالها ، اضافة الى تدريب الفنيين وتبادل الخبرات
بين البلاد العربية . ويتعاون المركز مع المنظمات العربيـــة
والدولية .

له مدير عام متفرغ .

يتألف مجلس الادارة من ممثل عن كل دولة عضو في المركز
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يصدر المركز نشرات (ن) وتقارير علمية (ت) توزع مجاناً
عند الطلب وبطريقة التبادل .

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أكساد