



## Quantitative Analysis of Soil Extracts with ICP-AES

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### 1 Introduction

The ICP technique is widely accepted in agricultural institutions for the determination of major and minor elements in soils and plants, heavy metal content in soils, receiving industrial waste and environmental monitoring of soils. It can also be used for the quality control of sites exposed to pollution and for research and development projects to improve plant growth. In this study, we will focus on ammonium acetate extracts of soils. Depending on the elements of interest, different extracts are used to simulate the uptake by the plant. Different digestion or extraction procedures will be reviewed.

### 2 Principle

#### 2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

#### 2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

### 3 Sample preparation

Two type of extractions were used:

#### 3.1 Acidic Ammonium Acetate EDTA Soil Extracts

Reagents:

50 mL of extractant solution per determination is prepared as follows: 38.5 g  $\text{NH}_4\text{CO}_2\text{CH}_3$ , 25 ml  $\text{CH}_3\text{CO}_2\text{H}$  (96%) and 29.225 g EDTA were diluted to 1 L.

Sample preparation:

5 g of dried soil sample weighed into a 250 mL polypropylene bottle is mixed with 50 ml of extractant solution. The suspension is shaken at 19-21 °C in a thermostatted water bath, laboratory shaker for one hour. The sample solution is filtered through folded filter paper (Mg free) and stored in a polypropylene bottle for ICP analysis. For good reproducibility of the results, it is important to keep the extraction conditions (soil/extractant ratio, temperature and duration of extraction) constant.

#### 3.2 HCl and $\text{HNO}_3$ Soil Extracts

Reagents:

Concentrated HCl (37%) and  $\text{HNO}_3$  (65%) analytical reagent grade acids.

Sample preparation:

2 g of milled soil (< 150  $\mu$  sieve) is digested with 15 mL (20 mL, if calcareous) of HCl (18.5% w/v) and 5 mL  $\text{HNO}_3$  (conc.). The samples were digested in tubes using a heated block over a 9 hr period using temperatures up to 130 °C and taken to dryness. The samples were redissolved in HCl and made to 100 mL with deionized water. The final solution was 5% HCl (v/v). It is also possible to make a microwave digestion.



## 4 Standards

Two distinct sets of standards were used; one for the major elements and the other for traces.

**Table 1: Standards prepared in Acetic Ammonium Acetate EDTA**

Concentration in g/kg					
Element	Std0	Std1	Std2	Std3	Std4
CaO	0	0.56	2.80	5.60	11.20
MgO	0	0.066	0.166	0.664	1.33
K <sub>2</sub> O	0	0.060	0.120	0.600	1.200
Na <sub>2</sub> O	0	0.0135	0.027	0.054	0.108

Concentration in mg/kg					
Element	Std0	Std1	Std2	Std3	Std4
Zn	5	10	50	100	150
Mn	10	50	100	200	300
Cu	5	10	50	100	150

**Table 2: Standards prepared in HCL/HNO<sub>3</sub>**

Concentration in mg/L for major elements					
Element	Std0	Std1	Std2	Std3	
Fe	0	70	100	150	
Mg	0	30	100	150	
Al	0	200	250	300	
Ca	0	700	500	150	

Concentration in mg/L for minor elements					
Element	Std0	Std1	Std2	Std3	
Zn	0	0.5	1	2	
Ni	0	0.1	0.2	0.5	
Cr	0	0.3	0.5	1.5	
Cu	0	0.1	0.3	1.5	

For soils, the following approximate matrix is used for the minor standards to improve accuracy:  
100 ppm Fe, 300 ppm Al, 400 ppm Ca, 100 ppm K and 50 ppm Mg

## 5 Instrument specification

The work was done on a PANORAMA. The specifications of this instrument are listed in table 3 and 4.

**Table 3: Specification of spectrometer**

Parameters	Specifications
Mounting	Paschen Runge
Focal length	0.5 m
Thermoregulation	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
1st order resolution	0.025 nm
2nd order resolution	0.012 nm
Order	2nd order

**Table 4: Specification of RF Generator**

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

## 6 Operating conditions

The operating conditions are listed in table 5 below.

**Table 5: Operating conditions**

Parameter	Condition
RF Generator power	1400 W
Plasma gas flowrate	18 L/min
Auxiliary gas flowrate	0.8 L/min
Sheath gas flowrate	0.15 L/min
Nebulizer gas flowrate	0.35 L/min
Nebulizer flowrate	1.2 bars (18 psi)
Sample uptake	0.3 mL/min
Type of nebulizer	Concentric
Type of spray chamber	Cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm



The use of the argon humidifier, a cross flow nebulizer and the large internal diameter (ID) injector tube enabled trouble free analyses, even with the high dissolved salts. The larger ID injector tube also ensures a minimization of interferences. Due to the high dissolved salts, an initial conditioning of the spray chamber is advised for maximum stability. It is also imperative to use matched standards or standard addition due to the viscosity of the solutions.

## 7 Discussion

Background correction has been used for both the major and minor elements for greater accuracy. This is because the matrix increases the background compared to water samples. An argon humidifier and a cross flow nebulizer were used to avoid clogging at the tip of the nebulizer, thus improving long term stability.

### 7.1 Acidic Ammonium Acetate EDTA Soil Extracts

**Table 6 : Sample results**

Analyte	Wavelength (nm)	Background correction (nm)	Sample Concentration
CaO	315.887	-0.068	1.41 g/kg
MgO	279.079	+0.055	0.113 g/kg
K <sub>2</sub> O	766.490	-0.071	0.130 g/kg
Na <sub>2</sub> O	589.592	+0.071	0.017 g/kg
Zn	213.856	-0.030	66.88 mg/kg
Mn	257.610	-0.030	41.34 mg/kg
Cu	324.754	+0.041	1.74 mg/kg

### 7.2 HCl/HNO<sub>3</sub> Acid Soil Digestion

**Table 7: results for BCR Soil Sample 141**

Analyte	Wavelength (nm)	Background Correction (nm)	Measured Value (mg/l)	True Value (mg/l)	Accuracy (%)
Fe	259.940	- 0.030	126.6	131	3.3
Mg	279.079	+ 0.055	36.3	36	0.8
Al	396.152	- 0.030	268.1	279	3.9
Ca	317.933	- 0.071	620.9	642	3.3
Zn	213.856	- 0.030	0.390	0.410	4.9
Ni	231.604	- 0.030	0.152	0.160	5
Cr	267.716	- 0.030	0.345	0.370	4.8
Cu	324.754	+ 0.041	0.244	0.228	7.3

## 8 Summary

The results are in good agreement with the expected values. Some care must be taken with the sample preparation, especially with soil extracts. To reduce matrix effects, radial viewing is preferred to axial. Furthermore, the standards were prepared with the same amount of acid or ammonium acetate used with the real samples, to have the same nebulization efficiency between standards and samples. Background correction was used to nearly remove spectral matrix effects. Two different sets of standards were used; one for major and the other for minor elements in order to be as accurate as possible. Sample throughput with simultaneous ICP spectrometers, such as the PANORAMA is very high, up to 60 samples in an hour.

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