

IMACIMUS APPLICATION FOR QUALITY CONTROL OF FERTILIZERS

ABSTRACT

In the precision agriculture is a core business to monitor crop nutritional information on-site. It is known that the quick and multiparametric analyzer system IMACIMUS allows to monitor the water and the nutrient uptake of the crop and provides growers on how to adjust their irrigation and fertilizers to the optimal level.

However, in this article we present a new application of the IMACIMUS equipment for quality control in the manufacture of the fertilizers themselves.

It is shown that with the analysis of known solutions of each fertilizer through the IMACIMUS probe, we get comparable results to those obtained by conventional but more expensive laboratory analysis.

We do directly measurements in mg/L (or mmol/L) for each ion and these values are easily transformed by means of a formula for any unit mineral component of the fertilizer to be compared with lab results.

Keywords: *quick analysis, multiparametric analysis, irrigation, water, nutrients, cations, anions, crop, minerals, fertilizers, quality control, production, fertilizer manufacturers, carbon nanotubes, nanotechnology, laboratory, real time, measurement, analytical, selectivity*

INTRODUCTION

The MultiION Kit, now so-called IMACIMUS MultiION is the nutrient analyzer Brand able to monitor the chemical needs of crops. NT Sensors for over 10 years helped clients around the world increase crop production, improve product quality and size, optimize fertilizer and water usage, and control of salinity.

Multiion probe is an electrode's holder. The probe can hold up to 7 modular electrodes or insert sensors.

These sensors are all-solid-state ion selective electrode based on a transducing single-walled carbon nanotubes.

The use of the carbon nanotechnology allows getting very short response time and because of their intrinsic advantages of miniaturization and straightforward fabrication, leads to an easy integration of several electrodes reaching multiple ion measurements at the same time.

IMACIMUS can perform directly measurement without being affected for colour, turbidity, presence of oxygen, redox potential or high concentration of the ions. Since the technique used is electrochemistry only free ions are measured, not chelated or non-dissolved species.

So, we can achieve up to 10 parameter results in a single minute with the IMACIMUS 10 equipment (Calcium, Chloride, Potassium, Sodium, Ammonium, Nitrate, Magnesium, pH, Electronic Conductivity and Water Hardness), having a high appreciated information in real time.

In addition to common uses in crops we are going to show you *a new and easy application for employ in the quality control on the production of fertilizers.*

APPLICATION

EXPERIMENTAL

Material:

IMACIMUS 10 Kit (multiionic and pH analyzer)
 pH buffers 4,01 and 7,00 UpH
 Standard calibration solutions HP08 (agriculture usual range)
 Solid samples of common fertilizers with composition and specifications

Sample Preparation:

IMACIMUS technique is based on electrochemistry, therefore sample must be as solution not solid.

By calculating from the specifications sheet of any fertilizer to ensure that the ionic determinations are within the range of the standards, the samples have been dissolved taking:

1000 mg (aprox.)* of fertilizer in 1 L in deionized water at room temperature

(*) It is only necessary to know the exact amount to make further calculations.

We would remark that stirring has been applied to dissolve samples and we would finally appreciate a small quantity of the solid (<5%) remaining undissolved at room temperature. By trying to heat the sample, it does not effect when the sample gets back the room temperature due to the low solubility of some Calcium and Magnesium minerals (phosphates, carbonates or oxides), especially the Calcium ones, at pH values around 7.

Sample Acidification:

In order to improve fertilizer dissolution we can acidify the previously diluted samples with hydrochloric acid 0,1 N.

We make some calculations and proceed by adding into the same volumetric flask of the first sample preparation, between 2,5% and 3,4% v/v of HCl 0,1 N to the aqueous samples. See in the table below the resulting values of pH (between 4,0 and 3,0 UpH).

It is important to acidify gently so as not to exceed the lower limits where the sensors can not work correctly.

Take into account that by acidifying resulting values of Chloride (increase), Nitrate (lose), Potassium (lose) and Ammonium (lose), will have some changes due to the concentrations of H^+ and Cl^- added to the solutions (same for Sodium but actually it doesn't exist). The losses were calculated to be between -16% and -32% in this experiment.

Same will occur with Calcium and Magnesium (see 'RESULTS AND DISCUSSION' bellow).

In case of the addition of 3,4% v/v we just see an optimal increase in solubility with a value of the pH=3, which is still correct for the operation of the sensors.



without acidification (pH≈6)

with acidification (pH≈3)

Analysis:

Use the IMACIMUS device as usual for measuring the sample in triplicate (n=3).

- Samples were determined as common samples on the scope and main uses for IMACIMUS (feel free to see guides at NT Sensors official web).
- No filtration or pretreatment is required.
- Same procedure for acidified samples.

RESULTS AND DISCUSSION

There was no interferences shown from the matrix with the analytical technique. Good repeatability of the sample (n=3) was obtained.

Sample results are shown as it are obtained from the equipment (mg/L or ppm) from the different parameters (after averaged n=3), as follows (in blue, samples being acidified):

Sample	Ca ²⁺	Cl ⁻	K ⁺	Na ⁺	NH ₄ ⁺	NO ₃ ⁻	Mg ²⁺	pH	Units
14-14-14	3,3	121	119	3,9	88	284	7,9	5,9	mg/L
14-14-14 Ac.	21	229	94	5,3	77	202	28	3,0	mg/L
13-9-19	2,2	11	149	2,0	94	302	2,9	6,0	mg/L
13-9-19 Ac.	20	130	112	3,0	74	239	17	3,0	mg/L
18-18-0	4,0	10	8,0	3,1	99	382	15	5,9	mg/L
18-18-10 Ac.	42	142	6,3	5,0	86	270	43	3,0	mg/L
28-0-0	7,1	8,4	5,3	0,4	117	789	4,3	7,6	mg/L
28-0-0 Ac.	24	85	5,0	0,4	116	534	16	4,0	mg/L

With the average obtained in mg/L (ppm) from the sample dissolved and employing a spreadsheet, we convert the original results from IMACIMUS in the units of % of weight (w/w), as we appear in the specifications or in the laboratory analysis reports too. Plus, available are different conversion for other units to be compared.

COMPLEX FERTILIZERS									
Sample		Mw K2O	Aw 2xK	Weight (mg/1 L)	IMACIMUS Result (mg/L Ion)	IMACIMUS Result (% w/w)	Lab Result (% w/w)	Rec (%)	pH
14-14-14	% K2O	94,2	78,2	1013	119	14,2%	14,3%	99%	5,9
		Mw MgO	Aw 1xMg						
	% MgO	40,31	24,31	1013	7,9	1,3%	3,4%	38%	5,9
	% MgO	40,31	24,31	1013	28	4,6%	3,4%	134%	3,0
		Mw CaO	Aw 1xCa						
	% CaO	56,08	40,08	1013	3,3	0,5%	0,0%	-	
	% CaO	56,08	40,08	1013	21	-	0,0%	-	3,0
		Aw N	Mw NH3						
	% N - NH3	14,01	17,03	1013	88	7,1%			
		Aw N	Mw NO3		N total	13,5%	14,7%	92%	5,9
13-9-19		Mw K2O	Aw 2xK						
	% K2O	94,2	78,2	1049	149	17,1%	18,4%	93%	6,0
		Mw MgO	Aw 1xMg						
	% MgO	40,31	24,31	1049	2,9	0,5%	1,8%	25%	6,0
	% MgO	40,31	24,31	1049	17	2,7%	1,8%	148%	3,0
		Aw N	Mw NH3						
	% N - NH3	14,01	17,03	1049	94	7,4%	8,0%	92%	6,0
		Aw N	Mw NO3		N total	13,9%	14,1%	98%	6,0
	% N - NO3	14,01	62,01	1049	302	6,5%	6,1%	107%	6,0
18-18-0		Mw CaO	Aw 1xCa						
	% CaO	56,08	40,08	1019	4	0,5%	4,0%	14%	5,9
	% CaO	56,08	40,08	1019	42	5,8%	4,0%	144%	3,0
		Mw MgO	Aw 1xMg						
	% MgO	40,31	24,31	1019	15	2,4%	4,8%	51%	5,9
	% MgO	40,31	24,31	1019	43	7,0%	4,8%	146%	3,0
		Aw N	Mw NH3						
	% N - NH3	14,01	17,03	1019	99	8,0%			
		Aw N	Mw NO3		N total	16,5%	17,8%	92%	5,9
	% N - NO3	14,01	62,01	1019	382	8,5%			
28-0-0		Mw CaO	Aw 1xCa						
	% CaO	56,08	40,08	1017	7,1	1,0%	6,8%	14%	7,6
	% CaO	56,08	40,08	1017	24	3,3%	6,8%	49%	4,0
		Mw MgO	Aw 1xMg						
	% MgO	40,31	24,31	1017	4,3	0,7%	4,4%	16%	7,6
	% MgO	40,31	24,31	1017	16	2,6%	4,4%	59%	4,0
		Aw N	Mw NH3						
	% N - NH3	14,01	17,03	1017	117	9,5%			
		Aw N	Mw NO3		N total	27,0%	27,1%	100%	7,6
	% N - NO3	14,01	62,01	1017	789	17,5%			

(Aw means Atomic weight and Mw means Molecular weight)

Within the last columns on the spreadsheet we can compare the results from IMACIMUS multiprobe and lab results. Looking at the values for monovalent ions (Potassium, Ammonium and Nitrate) the values are very closer against the lab ones, so a good reproducibility is assured.

For divalent ions it is necessary to look at the recovery (against lab information from the fertilizers)^{\$} to see the effect of the acidification and how to profit the values directly provided by the IMACIMUS multiprobe:

pH	Calcium recovery average ^{\$}	Magnesium recovery average ^{\$}
6,0	14%	32%
4,0	49%	59%
3,0	144%	143%

(^{\$}) mixed average (obtained from all analyzed fertilizers)

So, in the case of divalent ions a recovery factor that better correlates both results, IMACIMUS and lab, maybe could be determined by measuring a larger number of different samples from each class of fertilizer and appropriately adjusting pH context, *getting this especific correlation factor from the averaged samples of any particular class of fertilizer.*

CONCLUSIONS:

Looking at the values for monovalent ions (Potassium, Ammonium and Nitrate) the values are very closer against the lab ones, so a good reproducibility is assured and acidification was not needed.

For divalent ions (Calcium and Magnesium, also known as a minor elements) we obtain low results due to the not complete dissolution of their mineral salts around neutral pH, not in this case because of chelating agent contexts nor of some feasible interferences.

It is also shown that we can reach satisfactory recoveries for Calcium and Magnesium by gently acidifying the original diluted samples (process that is easy to do), leading to probably achieve good and precise correlation factors.

The standard solution calibrations HP08 have been shown to have the adequate performance for the intended purpose.

IMACIMUS device and sensors shown they reach laboratory performance as well.