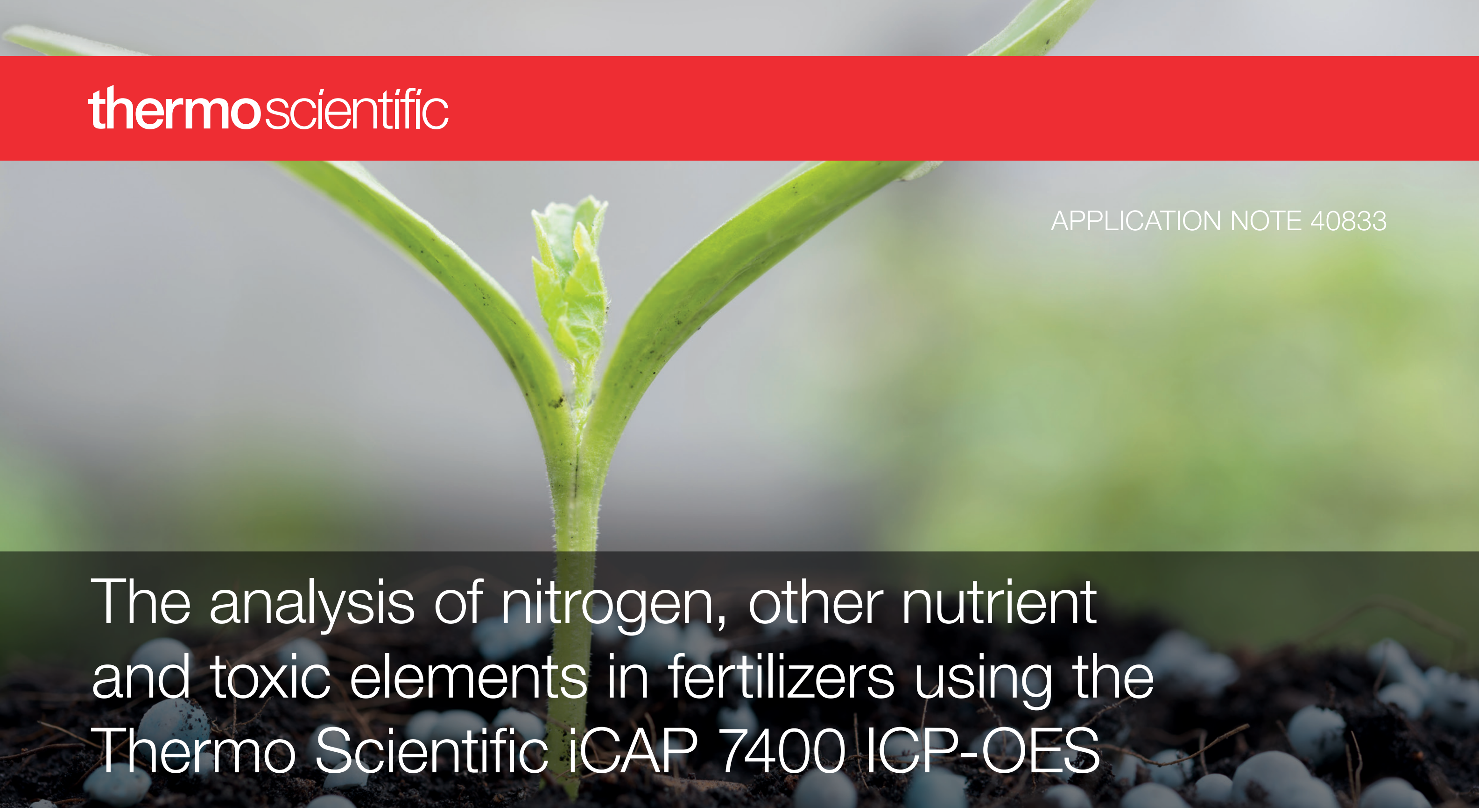

APPLICATION NOTE 40833

The analysis of nitrogen, other nutrient and toxic elements in fertilizers using the Thermo Scientific iCAP 7400 ICP-OES

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Goal

To demonstrate accurate analysis of nitrogen and other elements in fertilizers, using the Thermo Scientific iCAP 7400 ICP-OES Duo.

Introduction

Fertilizers are used to provide major plant nutrients (N, P, K), secondary plant nutrients (Ca, S, Mg) and micronutrients such as B, Mn, Fe, Cu, Zn, Mo and Se. Accurate determination of the composition of fertilizers is essential so that the correct dose can be applied to the soil. An insufficient application of a fertilizer may result in poor crop yield. In contrast, an excessive application may result in environmental damage such as eutrophication – caused by dissolved phosphates and nitrates entering water courses or land contamination from non-nutrient elements within the fertilizers. ICP-OES facilitates the cost effective analysis of fertilizers due to the powerful multi-element capability of this technique. The Thermo Scientific iCAP 7000 Plus Series ICP-OES enables the simultaneous analysis of all the plant nutrition elements (including nitrogen) as well as potential harmful elements (As, Cd, Cr) in fertilizers.

Instrumentation

The Thermo Scientific™ iCAP™ 7400 ICP-OES Duo was selected for this analysis due to the instruments ability to read signals from both the axial and radial plasma view, which enables both major constituents and trace elements to be effectively determined in the same sample. The Thermo Scientific iCAP 7000 Plus Series ICP-OES comprises of a range of high performance ICP-OES systems which enable high sample throughput, application flexibility and low cost of ownership. The range employs a high resolution Echelle spectrometer with an advanced Charge Injection Device (CID) detector. The advanced CID detector enables higher sensitivity and lower noise than any of its predecessors. The CID detector is also a non-blooming device and in this application it has the advantage of being able to measure high concentrations of major nutrient elements and low levels of micronutrient elements at the same time without saturation. The full wavelength coverage of the unique CID detector allows the optimum wavelength to be selected whilst the high sensitivity of the axial plasma view provides the lowest possible detection limits for this application.

Sample and standard preparation

Inter-laboratory performance check samples (MAGRUDER-Fertilizer check sample numbers 2003/08, 2004/10, 2005/04) were used during the analysis. The samples were well mixed to ensure homogeneity and then weighed (1 g) into a beaker. 20 mL of 18.5% hydrochloric acid was added to the beaker and the initial reaction was allowed to subside before being boiled for 10 minutes. The sample was filtered into a 100 mL volumetric flask and made up to volume with deionized water. A stock standard solution was prepared from a well characterized inter-laboratory performance sample using the same method that was used to prepare the samples. This was then diluted to the appropriate concentrations for the range of expected results. Additional nitrogen standards were prepared from ammonium dihydrogen orthophosphate using the same method used for the sample preparation, but replacing the 1 g of sample with an appropriate amount of ammonium dihydrogen phosphate.

All deionized water used was (as far as possible) free from nitrogen. This can be achieved by either boiling or bubbling an inert gas though the water. In this analysis the water was heated for 15 minutes, covered and allowed to cool before use.

Method development and analysis

Since the samples contained low amounts of total dissolved solids the standard aqueous sample introduction kit was used. Suitable wavelengths were selected for each of the elements of interest (Table 2). Using the Plasma Optimization function of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, the plasma parameters were optimized to produce a set of optimum parameters (Table 1) for the elements of interest, then the standards and samples were run. The subarray plots of each of the wavelengths were examined and the optimum wavelength and background correction points were selected. Figure 1 shows the subarray plot of the nitrogen peak at 174.272 nm for each of the samples analyzed. In this detailed view the integration area and the background correction points can be examined, and repositioned if necessary. A detection limit study was carried out by running a blank sample with ten replicates. The standard deviation of the replicates was multiplied by three to give the instrument detection limit (IDL). The IDL was then multiplied by the dilution factor (100x) to provide the method detection limit (MDL) of the element in the solid.

Table 1. Instrument and method parameters.

Parameter	Setting	
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white	
Pump Speed	50 rpm	
Nebulizer	Glass concentric	
Nebulizer Gas Flow	0.65 L·min^{-1}	
Spray Chamber	Glass cyclonic	
Auxiliary Gas Flow	0.5 L·min^{-1}	
Coolant Gas Flow	16 L·min^{-1}	
Center Tube	2 mm	
RF Power	1350 W	
Exposure Time	**Axial**	**Radial**
	UV 15 s, Vis 5 s	UV 8 s, Vis 3 s

Table 2. Element wavelengths and plasma view used as well as determined method detection limits.

Element and wavelength (nm)	View	MDL (mg·kg^{-1})
As 189.042	Axial	0.4
B 249.678	Radial	1
Ca 422.673	Radial	2
Cd 214.438	Axial	0.01
Co 238.892	Radial	0.4
Cr 267.716	Radial	0.3
Cu 324.751	Radial	0.6
Fe 259.94	Radial	0.6
K 766.49	Radial	20
Mg 285.213	Radial	0.3
Mn 259.373	Radial	0.09
Mo 202.03	Axial	0.02
N 174.272	Axial	250
Na 588.995	Radial	3
Ni 221.647	Axial	0.04
P 177.495	Radial	20
Pb 220.353	Axial	0.2
S 180.731	Radial	1
Se 196.09	Axial	0.2
Zn 202.548	Radial	0.09

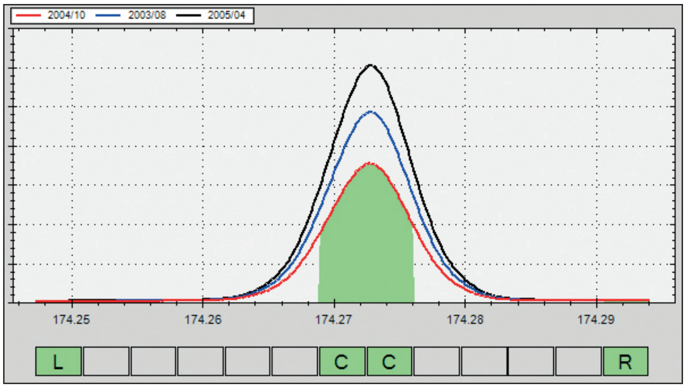

Figure 1. Subarray plot of N 174.272 nm.

Results

The instrument was calibrated and the samples run in one continuous run. The calibration plot for nitrogen is shown in Figure 2. Furthermore, it is possible to check the performance of the calibration standards on-screen by reviewing the associated correlation coefficient for the curve fit. The results of the analysis are shown in Table 3. Recoveries for nitrogen in all three reference materials are between 89 and 105%. Most other analytes exhibit recoveries within ±20% of the expected value. The determined method detection limits were sufficiently low to provide very good accuracy. Only in the case of As in the sample ID 2003/08 the certified concentration was at the same level like the MDL and could therefore not be quantified.

Table 3. Certified and found concentrations as well as calculated recovery for all three reference materials.

Analyte	Unit	2003/08			2004/10			2005/04		
		Certified	Found	Recovery (%)	Certified	Found	Recovery (%)	Certified	Found	Recovery (%)
As	mg·kg^{-1}	0.8	<MDL	ND	44.89	44.15	98.4	1.26	1.32	104.8
B	%	3.4	2.0	58.8	0.13	0.14	107.7	0.004	0.004	100.0
Ca	%	1.12	1.12	100.0	6.49	6.39	98.5	0.14	0.14	100.0
Cd	mg·kg^{-1}	2.17	2.2	101.4	1.15	1	87.0	0.74	0.87	117.6
Co	mg·kg^{-1}	6.91	6.21	89.9	56.86	52.28	91.9	7.61	4.94	64.9
Cr	mg·kg^{-1}	54.19	59.29	109.4	185.12	178.16	96.2	8.58	11.13	129.7
Cu	%	0.004	0.004	100.0	0.12	0.11	91.7	0.002	0.002	100.0
Fe	%	0.86	0.89	103.5	0.47	0.43	91.5	1.1	1.01	91.8
K_2O (K)	%	18.3	19.08	104.3	18.65	18.24	97.8	4.1	4.33	105.6
Mg	%	0.95	0.92	96.8	2.21	2.06	93.2	0.14	0.12	85.7
Mn	%	0.16	0.16	100.0	1.53	1.33	86.9	0.55	0.52	94.5
Mo	mg·kg^{-1}	4.75	4.04	85.1	14.33	12.07	84.2	0.74	1.37	185.1
N	%	15.83	15.85	100.1	3.46	3.08	89.0	29.36	30.65	104.4
Na	%	0.1	0.11	110.0	0.56	0.6	107.1	0.04	0.04	100.0
Ni	mg·kg^{-1}	26.28	24.75	94.2	89.67	75.75	84.5	6.81	8.76	128.6
P_2O_5 (P)	%	4.73	4.72	99.8	9.71	9.04	93.1	2.97	3.08	103.7
Pb	mg·kg^{-1}	8.63	7.95	92.1	21.64	21.91	101.2	3.07	2.42	78.8
S	%	12.72	12.58	98.9	8.03	8.15	101.5	9.37	9.54	101.8
Se	mg·kg^{-1}	1.79	0.31	17.3	2.47	2.09	84.6	1.19	1.01	84.9
Zn	%	0.024	0.028	116.7	0.452	0.452	100.0	0.01	0.01	100.0

<MDL: Found concentration below the method detection limit.

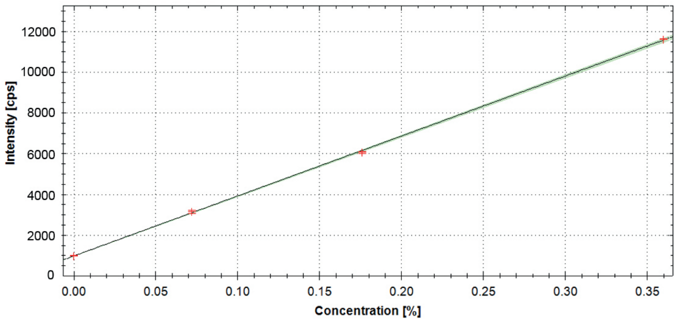

Figure 2. Calibration curve for N 174.272 nm with an R^2 of 0.9998.

Conclusion

In conclusion, all of the results obtained using the Thermo Scientific iCAP 7400 Duo ICP-OES are in alignment with the mean results (within 2 standard deviations of the mean) of certified values. Any exceptions to these results have occurred if the certified value was calculated from results submitted from less than 5 laboratories (leading to inaccurate statistics) or if a different method was used to determine the results. In these cases, the results obtained on an iCAP 7000 Plus Series ICP-OES are approaching 2 standard deviations of the mean.

The elements with data calculated from less than 5 laboratories are As, B and Se in sample ID 2003/08, Se in sample ID 2004/10 and Se in sample ID 2005/04. The analysis of nitrogen was carried out in the axial view, which enabled excellent instrument detection limits (2.5 ppm) and a typical RSD of 0.2% at N 174.272 nm with an EMT Duo torch. There was no requirement to use expensive modified or custom torches that exclude atmospheric nitrogen from the plasma. Furthermore, no ionization buffer was used during the analysis, so the torch life time will be maximized. The Thermo Scientific Qtegra ISDS Software enables correction factors to be entered in to a method so that an element result can be corrected and reported as a compound i.e. P as P_2O_5 or K as K_2O. The iCAP 7400 ICP-OES Duo enables simultaneous analysis for all of the elements reported. In addition, the instrument also offers the best analysis solution for the sample matrix analyzed. The radial view allows for the analysis of major elements and the axial view allows for the analysis of trace elements.

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