

## ICP-MS: A powerful tool for quantifying toxic trace elements in wheat germplasm evaluation

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**ABSTRACT:** Analysis of toxic trace elements in food crops is receiving increasing attention because of the growing public and scientific awareness of the environmental issues. In general, the role of these elements in relation to wheat quality has been overlooked and considered to be of minor significance, with cadmium being the exception. Perhaps one reason for the lack of this interest was because researchers were unable to monitor the minute quantities due to unavailability of rapid and sufficiently sensitive analytical techniques. The advent of ICP-MS for multi-element analysis confers the ability to analyze up to 90% of the elements of the Periodic Table in less than a minute to sub ng/g (ppb) level. In order to check the application of the technique in wheat germplasm evaluation we screened several wild and domestic wheat lines for 65 elements. Among them the concentration of 27 elements were found above the blank levels. Cadmium levels varied between zero and 0.3 mg/kg. The other harmful elements detected are Al, Sb, As, Cu, Cr, Pb, Ni, Se, Sn, Th, U, V, and Zn.

**INTRODUCTION:** Intensive use of agro-chemicals in modern farming practices and indiscriminate dumping of industrial and municipal wastes containing toxic elements have become a worldwide potential source of food crops contamination. Since the inorganic toxins are not biodegradable, they can accumulate in the food chain and present a threat to crop quality as well human and animal health (Underwood, Trace Elements in Human and Animal Nutrition, 3rd Edn. Academic Press, 1971; Adriano, Trace Elements in the Terrestrial Environment, 1986; Tiller, Heavy Metals in Soils and Their Environmental Significance, 1989; Fergusson, The Heavy Elements: Chemistry, Environmental Impact, and Health Effects, 1990). Traditionally the research related to wheat quality has been concerned primarily with essential elements. However, the literature on various toxic trace elements (except Cd) is relatively scarce. The lack of such information has mainly been because of limitations of available analytical techniques such as AAS, ICP-AES, and INAA. Particularly for analysis of biological samples, all of these suffer from significant drawbacks, e.g. slowness, detection limits, multi-elements capability and interferences. Furthermore, the sensitivity of these techniques varies widely across the periodic table. The low detection limits and high speed multi-element analysis capacity of ICP-MS are opening up wholly new areas of research on essential and toxic elements in the field of environmental science. Advantages of ICP-MS for multi-element analysis have been described in numerous articles and review chapters (e.g., Jarvis et al., Handbook of ICP-MS, 1992). In this paper the suitability of ICP-MS for multi-elements analysis in wheat germplasm evaluation has been assessed.

**EXPERIMENTAL:** Dried seeds were powdered in a clean agate mortar and pestle, which was cleaned using 5% HNO<sub>3</sub> and ultrapure water. 0.5 g aliquots were placed in a 15 ml screw capped Teflon beaker. 3 ml concentrated HNO<sub>3</sub> and 2 ml HF were added to the sample and the beaker was placed on a hot plate at a temperature of 100°C overnight, then evaporated to dryness. To the

dried mass 2 ml of  $\text{HNO}_3$  followed by 25 drops of  $\text{H}_2\text{O}_2$  were added in drops to minimize foaming and then evaporated to near dryness. After three repetitions of the  $\text{HNO}_3/\text{H}_2\text{O}_2$  procedure, samples were allowed to cool and made up gravimetrically with 2%  $\text{HNO}_3$  to approximately 100 g.

For digestion of wheat samples in a microwave oven (CEM, MDS 2000) about 0.25g of finally ground samples were placed into lined digestion vessels and the samples were wetted with 2 ml of nanopure (18 meg) water and 5 ml of concentrated  $\text{HNO}_3$ . The vessels were sealed and subjected to microwave heating with the pressure controlled at 80 psi for 8 min followed by 100 psi for 20 min. After the vessels were cooled to room temperature, 2 ml of concentrated HF was added, vessels sealed and subjected to Microwave heating using 100 psi for 20 min to digest any silicate material. The samples were dried on a hot plate to remove HF. Then, 3 ml of Concentrated  $\text{HNO}_3$  was added and the samples were dried once more. The final solutions were made in ca. 50 g of 2%  $\text{HNO}_3$ . In the microwave digestion procedure, use of  $\text{H}_2\text{O}_2$  was found to be unnecessary.

A VG Elemental PlasmaQuad model PQ2-STE ICP-MS was used for all data acquisition. Single element standard solutions purchased from Inorganic ventures Inc. (Lakewood, NJ) were utilized to prepare calibration and internal standards solutions. Analyses were performed using an external calibration procedure and internal standards were included for matrix and instrumental drift corrections. For data reduction the raw intensities were corrected for background counts, instrumental drift, matrix effects, and wherever applicable for molecular interferences. Procedural blanks were analyzed to check for any contribution from the reagents and/or digestion vessels.

**RESULTS AND DISCUSSION:** The HF/ $\text{HNO}_3$  digestion procedure seems to work well for wheat samples. Friel et al. (Analyst, 115, 1990), however, pointed out that where decomposition of organic-rich samples by hot plate digestion procedure may appear complete from the color and turbidity of the solution, small amounts of undecomposed organic matter may still remain in the solution which may interfere with the instrumental sensitivity. Based on indium counts we observed about 12% drift over a 12 hour run, which is considered normal drift for our instrument. Microwave digestion has been used successfully for dissolution of plant material (Dolan et al., Anal. Chem., 336, 99, 1990). We compared the performance of the instrument by analyzing the hot plate and microwave digested samples and found no significant difference in terms of instrumental sensitivity. However, the microwave digestion is much quicker and has advantages over hot plate digestion for economizing on time.

The accuracy of the procedure was assessed using the durum wheat flour (SRM 8436), a reference material certified by the National Institute of Standards and Technology (NIST), Gaithersburg, USA (Figure 1). The samples and standard were analyzed by ICP-MS for 65 elements and abundances for 27 of these elements are presented in Table 1. Since the concentration of other elements was found at the blank levels, the data for those elements are not presented here. Furthermore, the blank level for Cr was unusually high placing the Cr abundance in SRM 8436 below our detection limit of 0.1 mg/kg. However, the abundances in the wheat samples are above this detection limit, so Cr is included in Table 1. Please note that ICP-MS can scan the sample for 65 elements in about a minute and measures the concentrations accurately for the majority of these elements below ppb (ug/kg) level (see detection limits in Table 1). The results obtained by ICP-MS for SRM 8436 are presented in Table 1 and Figure 1 and are in agreement with the certified values for most of the elements, except Cr which was below our present detection limit and future studies of this type will work to lower this detection limit. Calibration based on internal standardization works well for obtaining the accuracy within 10%. However, more accurate results can be obtained by standard addition (Longerich et al., Chem. Geol., 93, 105, 1990) and isotope dilution (Beauchemin et al., Anal. Chem., 60, 687, 1988) but require additional measurements and are time consuming and also adds to experimental cost.

We analyzed more than 100 wheat samples collected from various parts of the world for 65

Table 1 Elemental Composition of Durum Wheat Reference Material and Wheat Germplasms (mg/kg)

Elements	SRM 8436		Samples			Detection Limit ( $\mu\text{g}/\text{kg}$ )
	Analyzed	Recommended	S1	S2	S3	
Mg	1109	1070	1847	1372	1133	0.257
Al	12.3	11.7	3.84	9.19	15.6	0.191
P	2723	2900	4607	5156	3127	8.87
Ca	287	278	332	998	796	3.85
Ti	4.21	5	12.6	17.4	13.7	0.164
V	0.027	0.021	0.006	0.054	0.359	0.024
Cr	0.058	0.023	0.315	0.405	0.727	0.102
Mn	14.93	16	41.8	15.8	18.4	0.024
Fe	43.3	41.5	54.0	82.3	57.9	2.92
Co	0.009	0.008	0.011	0.235	0.168	0.009
Ni	0.192	0.17	0.193	2.60	2.85	0.117
Cu	4.31	4.3	4.3	7.64	6.16	0.180
Zn	20.4	22.2	21.2	34.5	34.8	0.193
As	0.023	0.03	0.022	0.037	0.128	0.033
Se	1.28	1.23	1.69	2.41	1.93	1.10
Rb	1.84	2	2.44	5.75	6.31	0.067
Sr	1.17	1.19	2.09	2.02	3.54	0.105
Mo	0.739	0.7	1.03	36.2	2.17	0.039
Cd	0.108	0.11	0.273	0.127	0.008	0.011
Sn	0.051	—	0.397	0.204	0.163	0.036
Sb	0.015	—	nd	0.006	nd	0.009
Ba	2.07	2.11	6.12	0.934	7.28	0.099
Tl	0.001	—	nd	0.001	0.003	0.003
Pb	0.029	0.023	0.013	0.013	0.091	0.009
Bi	0.002	—	0.003	nd	nd	0.009
Th	0.007	—	0.033	0.021	0.038	0.007
U	0.002	—	nd	0.049	0.008	0.006

nd = not detected

elements. A representative results of three samples are presented in Table 1 and Figure 2. It is evident from the data that there is a genotype difference in terms of the elemental composition of the wheat samples. Sample S3 is low in Cd level but has other toxic elements in higher concentrations compared to Samples S1 and S2. Since durum wheat is an important food plant the presence of any toxic element is undesirable. Ericksson (Water, Air, and Soil Pollution, 53, 1990) pointed out that soil properties play an important role on uptake of toxic elements in plants. The uptake may also be affected by synergistic effects of other elements present in soil. Rapid multi-element determination in the soil-plant system will help in establishing the role of other elements on the uptake of toxic elements and ultimately wheat germplasm quality in various environmental settings. ICP-MS appears to be an ideal technique for this purpose.

Figure 1

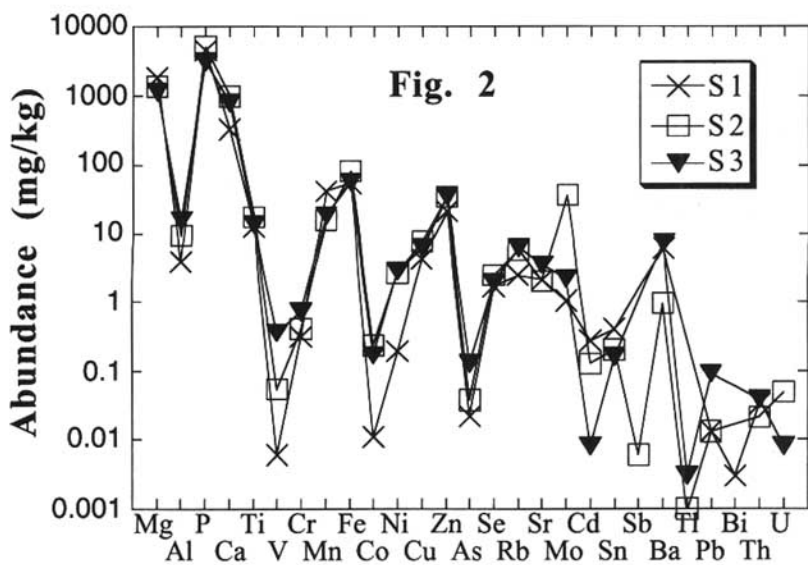
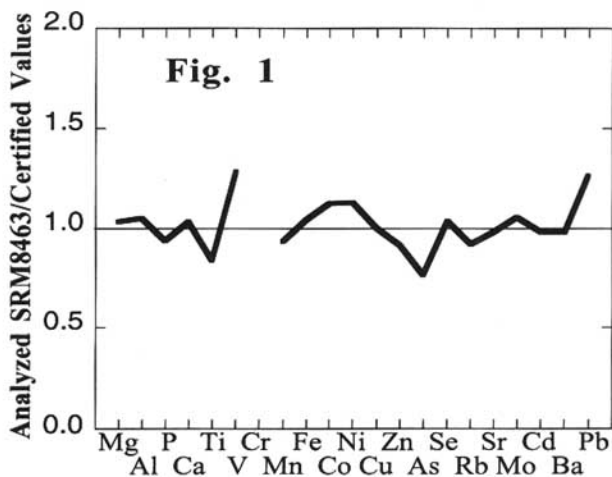


Figure 2