

# Concentrations of 63 Major and Trace Elements in Danish Agricultural Crops Measured by Inductively Coupled Plasma Mass Spectrometry. 1. Onion (*Allium cepa* Hysam)

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One-hundred-ten samples of onion (*Allium cepa* Hysam) from 11 Danish sites (10 onions from each site) uncontaminated by human activities other than normal agricultural practices were collected and analyzed for 63 major and trace elements using a newly developed high-resolution inductively coupled plasma mass spectrometry method. Sample handling, sample preparation, and analysis of the samples were performed under carefully controlled contamination-free conditions. Mean concentrations of the elements (micrograms per kilogram of fresh weight) were compared with those reported previously from other surveys. The results provide useful biological and nutritional information on onions.

**Keywords:** *Onion (Allium cepa Hysam); HR-ICP-MS; major elements; trace elements; multielemental analysis*

## INTRODUCTION

Quantitative determinations of major and trace elements in agricultural crops are important in regard to environmental impact, nutritional effects, and geochemical exploration. The role of essential and toxic elements has attracted the attention of national institutes of many countries and spurred international organizations to assess the adequacy of major and trace elements and the safety of human food chain resources.

Very little is known about the concentrations of major and trace elements in onions. In a number of countries, surveys of trace elements such as Fe, Cu, Mn, Zn, Mo, Co, Ni, Cr, As, B, Rb, Br, Cd, Pb, and Hg in various crops including onion have been carried out. Extensive studies were reported from Sweden (Fuchs et al., 1976), Denmark (Hansen and Andersen, 1982; Levnedsmidtstyrelsen, 1995), Finland (Varo et al., 1980; Tahvonen and Kumpulainen, 1991), the United States (Wolnik et al., 1985), and Great Britain (Ward and Savage, 1994). In the past two decades, due to improvements in analytical techniques, the status of many trace elements has changed from nonessential to essential or from nontoxic to potentially toxic (Markert, 1993). Elements not detectable by older techniques (noble and rare earth elements) have now been found in quantitative amounts in crops by the use of modern analytical methods and instrumentation such as electrothermal atomization atomic absorption spectrometry (ETA-AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). However, the great diversity of sample

genotypes, sample preparation, and analytical methods involved in the determination of trace elements in agricultural crops makes the intercomparison of the results reported in the scientific literature very difficult.

High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is a powerful technique for trace and ultratrace analysis of biological materials offering rapid multielement analysis with excellent detection limits (Begerow and Dunemann, 1996). The use of a magnetic sector field mass spectrometer where the detector is off-line relative to the argon plasma ensures a very low background signal and therefore also very low detection limits. The possibility of using a mass resolution in the range of 400–10 000 makes it possible to resolve analyte peaks from many of the polyatomic interferences known from quadrupole ICP-MS and thereby significantly improve the detection of many elements; for example,  $^{52}\text{Cr}^+$  can be separated from  $^{40}\text{Ar}^{12}\text{C}^+$ . These facts make HR-ICP-MS a very attractive technique for multielemental determinations in various matrixes. The 63 elements measured in this study are those for which a routine HR-ICP-MS method could be applied. The number of elements possible to measure is dependent on the composition of the sample matrix and on the concentration of the individual element and may therefore vary from matrix to matrix.

The present study is a part of an ongoing Danish Food and Technology Development Program (FØTEK). The purpose of our study is to develop high-quality data on the levels of trace and major elements in selected crops produced by intensive cultivation with the use of fertilizer and pesticides. Second, these data will be used to relate trace element levels to agricultural production procedures and to gain information on the levels of mainly trace elements in crops to evaluate their role in the food chain.

The crops selected are those that constitute a large portion of the human diet. An attempt was also made to include different types of leaf or root vegetables,

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legumes, and various grain samples. Special care was taken in the selection of sampling sites and in the processes of sampling, packaging, and shipment to avoid contamination from external sources. Sample preparation and analysis were performed under clean room facilities. This paper presents the results for onions. Corresponding soil samples were also collected from each site. Soil-crop correlations will be reported later.

## MATERIALS AND METHODS

**Sites.** Eleven farms from Funen and mid-Jutland in Denmark were surveyed. The sites were selected to avoid contamination from human activities, such as highways, big cities, and factories, because they may affect the trace element levels in soils and crops. The sites were therefore >10 km from industries with extensive emission, at least 15 km from highways, 3 km from major roads, and 3 km from cities with >10 000 inhabitants. Only one site was located as near as 4 km from a galvanization industry. Similarly, onions from end rows and other areas where large quantities of fertilizers could have been deposited were not sampled.

**Sampling and Sample Preparation.** The same area of bed was sampled for both soil and onions. To avoid contamination of samples with the elements, laboratory modification, sampling device, special equipment for sample preparation, laboratory ware, and cleaning procedure were used in accordance with procedures outlined below.

**Onion.** Onions were harvested manually and allowed to weather for 1 week on the soil surface. Ten undamaged, healthy, average sized and normal shaped onions (*Allium cepa* Hysam) were sampled evenly across each site. All onion samples were collected with Nitrilite gloves (Nitrilite, powder free, Ansell Edmont), loose soil and stalk were shaken off, and thereafter the onions were placed in a polyethylene tissue bag with closing tape. The collected onions were sent to a drying room with shelter from the rain but open to the wind, to maintain natural drying conditions, where they were dried for a period of >2 weeks. This drying procedure is similar to the normal drying procedure for basket onions in Denmark.

To eliminate or at least minimize the risk of contamination, all sample preparations were performed under controlled condition in three rooms with lock-gate connection. The rooms are classified as R1 (ordinary condition), R2 (fairly clean), and R3 (clean, class 1000 room).

All sample preparations after the cleaning procedures were carried out in the class 1000 environment (R3). Disposable surgical latex gloves (Gammex, sterile and powder free, Ansell Edmont) and full laboratory dress (Tyvek) were worn throughout the procedure. Laboratory wares were stored in a clean air environment (R3).

In R1 the onion sample (1 onion = 1 sample) was cut from both ends ( $\approx 1$  mm) with a nitride-hardened titanium knife on a polycarbonate carving board, the outer layer was peeled off, and all 10 samples from one site were placed in a poly(ethylene terephthalate) (PET) bag. The sample was then passed through a lock into R2. The above-described R1 procedure was repeated in R2 and R3. In R3, the onion sample was quartered and homogenized in a blender (EVA, type 267732, DK) modified with a nitride-hardened titanium cutter.

**Soils.** A composite sample was collected at each site after onions were harvested as follows: Twenty cores (7.5 cm diameter and 25 cm deep) were taken from each site and those from each site mixed. Samples were air-dried and the coarse materials crushed using a quartz roller and then sieved (2 mm) to remove stones and plant debris. In this material texture, pH and total C were determined.

**Chemical Analysis.** *Onion.* The onion samples were digested with redistilled nitric acid (Merck p.a. subboiled in R3) in a microwave oven (MDS 2000, CEM Co., Matthews, NC) equipped with 12 closed Teflon PFA (perfluoroalkoxy) digestion vessels (CEM Co.). From the homogenized sample of one onion a mass of  $\approx 2$  g was accurately weighed (to the nearest 0.0001 g) into each vessel, and 10.0 mL of redistilled nitric acid (Merck

**Table 1. Instrumental Conditions for Plasma Trace 2 (HR-ICP-MS)**

RF power/W	1350
gas flow rates/L min <sup>-1</sup>	
plasma	12.5
auxiliary	1.5
nebulizer	0.920–0.980 (adjusted daily to max signal intensity)
sample uptake rate/mL min <sup>-1</sup>	0.7
ion sampling depth	adjusted to max signal intensity
ion lens settings	adjusted to max signal intensity
sampling cone	nickel, 1.0 mm orifice diameter
skimmer cone	nickel, 0.7 mm orifice diameter
Acquisition Parameters	
resolution 400	
peak widths	3
points/peak width	20
dwelt time/ms	10
scans	2 ( <sup>7</sup> Li, <sup>9</sup> Be, <sup>11</sup> B, <sup>79</sup> Br, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>89</sup> Y, <sup>90</sup> Zr, <sup>93</sup> Nb, <sup>98</sup> Mo, <sup>107</sup> Ag, <sup>111</sup> Cd, <sup>115</sup> In, <sup>118</sup> Sn, <sup>121</sup> Sb, <sup>126</sup> Te, <sup>133</sup> Cs, <sup>138</sup> Ba, <sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>146</sup> Nd, <sup>178</sup> Hf, <sup>182</sup> W, <sup>195</sup> Pt, <sup>197</sup> Au, <sup>202</sup> Hg, <sup>205</sup> Tl, <sup>208</sup> Pb, <sup>209</sup> Bi, <sup>232</sup> Th)
	1 ( <sup>101</sup> Ru, <sup>157</sup> Gd, <sup>159</sup> Tb, <sup>163</sup> Dy, <sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>172</sup> Yb, <sup>175</sup> Lu, <sup>185</sup> Re, <sup>193</sup> Ir, <sup>238</sup> U)
resolution 4000	
peak width	3
points/peak width	20
scans	2
dwelt time/ms	10 ( <sup>24</sup> Mg, <sup>28</sup> Si, <sup>31</sup> P, <sup>34</sup> S, <sup>44</sup> Ca, <sup>48</sup> Ti)
	20 ( <sup>45</sup> Sc, <sup>51</sup> V, <sup>52</sup> Cr, <sup>55</sup> Mn, <sup>56</sup> Fe, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>69</sup> Ga)
	30 ( <sup>27</sup> Al)
resolution 10000	
peak width	5
points/peak width	20
dwelt time 10 ms, 2 scans	<sup>23</sup> Na, <sup>39</sup> K
dwelt time 40 ms, 1 scan	<sup>153</sup> Eu
dwelt time 50 ms, 2 scans	<sup>72</sup> Ge

p.a. subboiled in R3) was added. The microwave oven (power level = 504 W) was programmed to run at increasing pressure of 40, 85, and 175 psi in three steps. The pressure was held constant for 3, 3, and 5 min during the three steps, respectively. The clear light yellow digest without any residue was then cooled to room temperature and transferred quantitatively to a 50 mL polyethylene flask, and double-deionized water (see description below) was added to a mass of  $\approx 30$  g (weighed to the nearest 0.0001 g). These sample solutions were stored at 5 °C until analysis. Two grams (weighed to the nearest 0.0001 g) of the sample solution was diluted with double-deionized water to 10 g (weighed to the nearest 0.0001 g) for the HR-ICP-MS measurement. Each batch consisted of 10 samples, a reagent blank, and a reference material (leek in-house material from the National Food Agency of Denmark). The reagent blank was used to evaluate contamination from digestion vessels and reagents, whereas the reference material was used to check the efficiency of the digestion to secure uniformity of the sample solution matrixes from batch to batch. The precision and accuracy of the analytical method were determined by 10 subsamples from one onion and 10 samples of reference material, respectively. Element concentrations for some of the samples were estimated in analytical combination with different spiked samples to verify that the sample solution matrix is similar for different onions, when the digestion condition is the same.

HR-ICP-MS (PlasmaTrace2, Micromass, U.K.) was used to determine 63 elements (Ag, Al, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir,

**Table 2. Elements in Onion (Micrograms per Kilogram, Fresh Weight)**

element	<i>n</i>	mean	median	min	max	BEC <sup>a</sup>	DL <sup>b</sup>
Ag	100	0.65	0.56	0.096	1.88	0.074	0.00071
Al	98	250	150	49	1230	5.8	0.097
Au	91	1.35	0.82	0.196	11.7	0.159	0.0020
B	102	1590	1660	340	3800	350	0.22
Ba	102	114	79	18.2	450	0.34	0.036
Be	86	0.033	0.024	b > c <sup>c</sup>	0.141	0.021	0.00032
Bi	100	0.086	0.080	0.0112	0.29	0.0094	0.000170
Ca	98	197000	176000	287000	410000	1200*	0.65
Cd	100	22	17.5	4.9	84	0.57	0.0047
Ce	100	2.3	1.83	b > c	8.0	3.12	0.038
Co	100	1.84	1.51	0.119	5.1	0.47	0.0070
Cr	102	9.6	8.35	1.86	47	0.52	0.028
Cs	81	0.21	0.116	b > c	0.98	0.74	0.00130
Cu	102	500	510	200	1010	0.75	0.030
Dy	102	0.0170	0.0105	b > c	0.143	0.00082	0.00070
Er	102	0.00065	b > c	b > c	0.054	0.026	0.00070
Eu	82	0.32	0.145	b > c	3.6	0.050	0.00090
Fe	101	2600	2600	1330	5200	10.3	0.21
Ga	99	0.22	0.138	0.0060	1.70	0.0082	0.00029
Gd	101	0.050	0.036	b > c	0.28	0.0133	0.0022
Ge	62	11.5	9.8	0.48	26	0.47	0.0130
Hf	71	0.84	0.314	b > c	10	0.043	0.00190
Hg	72	12.5	12.7	5.6	18.9	3.43	0.029
Ho	102	0.0025	0.00132	b > c	0.026	0.00108	0.000100
In	98	0.42	0.33	b > c	2.5	0.084	0.00130
Ir	93	0.033	0.0183	b > c	0.32	0.0192	0.00047
K	105	1640000	1630000	200000	3700000	910000*	290
La	85	0.21	0.124	0.026	0.93	0.0070	0.019
Li	89	0.64	b > c	b > c	5.2	0.78	0.0035
Lu	102	b > c	b > c	b > c	0.034	0.0053	0.000190
Mg	106	100000	10000	69000	166000	340*	0.110
Mn	102	1570	1450	490	3600	1.17	0.0100
Mo	78	8.0	6.6	b > c	32	8.2	0.30
Na	98	210000	169000	78000	500000	200000*	58
Nb	90	1.40	1.08	b > c	6.9	0.37	0.0059
Nd	101	0.174	0.101	b > c	1.02	0.0035	0.0110
P	108	440000	440000	240000	660000	1630*	0.24
Pb	99	6.2	5.4	1.22	19.7	0.40	0.023
Pr	101	0.034	0.0151	b > c	0.29	0.059	0.0041
Pt	88	0.20	0.102	b > c	1.74	0.067	0.00090
Rb	102	380	330	96	880	14.0	0.025
Re	98	0.0143	0.0073	b > c	0.124	0.0086	0.00051
Ru	99	0.161	0.110	b > c	1.10	0.22	0.0028
S	108	1230000	1260000	560000	2400000	177000*	17.8
Sb	102	1.79	1.70	0.162	4.6	0.069	0.00110
Sc	97	1.66	1.48	0.22	5.0	0.0122	0.00031
Si	97	11000	8800	3200	36000	7300*	0.42
Sm	102	0.044	0.039	b > c	0.20	0.00040	0.00020
Sn	98	3.5	3.6	0.90	8.4	0.82	0.0046
Sr	102	910	780	191	3100	0.42	0.0120
Tb	102	0.0069	0.0049	b > c	0.051	0.0056	0.00060
Te	83	2.2	2.3	0.52	4.9	0.61	0.0031
Th	98	1.05	0.81	0.29	5.2	0.0135	0.00048
Ti	99	910	740	105	2500	50	8.8
Tl	101	0.70	0.47	0.089	2.6	0.041	0.00021
Tm	102	0.0048	0.0039	b > c	0.0177	0.000012	0.000080
U	90	0.046	0.031	0.000161	0.26	0.0048	0.000180
V	82	0.44	0.43	0.111	1.03	0.024	0.0039
W	64	16.7	15	6.3	39	0.69	0.0180
Y	99	0.22	0.183	0.027	0.74	0.0067	0.0048
Yb	102	0.0048	0.00046	b > c	0.059	0.0036	0.00022
Zn	101	3400	2900	1450	10000	132	5.4
Zr	82	3.1	2.3	0.32	10.9	0.100	0.0049

<sup>a</sup> BEC, background equivalent concentration = mean of concentrations of the elements in 10 rpt blanks × individual dilution factor (≈70). \* Dilution factor (≈2600). <sup>b</sup> DL, detection limit = 3 times the standard deviation of 10 rpt of blanks analyzed as a sample. <sup>c</sup> b > c, element concentration below the mean of 10 blanks.

K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, P, Pb, Pr, Pt, Rb, Re, Ru, S, Sb, Sc, Si, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr) in the onion samples. These are the elements that we found possible to measure using a routine HR-ICP-MS method. The plasma conditions and acquisition parameters are summarized in Table 1. The isotopes analyzed are chosen to obtain the best possible sensitivity (highest natural abundance) and to avoid overlap from polyatomic

interferences. Where overlap from polyatomic ions could not be avoided, a higher resolution (defined as  $m/\Delta m$ ) of either 4000 or 10 000 was applied to resolve the analyte peaks from the otherwise interfering polyatomic peaks; for example,  $^{56}\text{Fe}^+$  can be separated from  $^{40}\text{Ar}^{16}\text{O}^+$  ( $\Delta m = 0.0049$  amu) using a resolution of 4000. When a higher resolution is applied, the ion transmission is decreased significantly; at resolutions of 4000 and 10 000 the transmissions are approximately 15% and

**Table 3. Some Properties of the Surface Soil (0–25 cm) at 11 Sites<sup>a</sup>**

site	field texture of surface			pH (CaCl <sub>2</sub> )	organic C/%
	sand/%	silt/%	clay/%		
1	71.5	21.1	5.4	7.0	1.19
2	66.1	13.5	7.7	7.6	2.1
3	88.8	5.4	4.2	6.1	0.88
4	68.6	23.6	5.9	5.6	1.09
5	85.6	5.7	4.3	5.5	2.6
6	63.1	26.2	8.5	6.8	1.26
7	58.1	29.1	10.8	6.6	1.16
8	64.8	24.6	8.2	6.4	1.42
9	64.2	25.7	8.2	7.0	1.09
10	50.3	42.3	4.2	7.2	1.27
11	66.1	21.8	10.1	6.6	1.17

<sup>a</sup> Soil texture: sand (0.063–2.0 mm), silt (0.002–0.063 mm) and clay (<0.002 mm).

1%, respectively. During the method development arsenic and selenium were also measured, but it was not possible to set up a reliable method for the determination of these two elements in onions. Even though the arsenic signal (<sup>75</sup>As<sup>+</sup>) can be separated from the interfering argonchlorid signal (<sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>) using a resolution of 10 000, the content of arsenic in the onions was too low to be measured reliably given the low ion transmission at resolution 10 000. For selenium the major isotope (<sup>80</sup>Se<sup>+</sup>) is interfered with by the argon dimer (<sup>40</sup>Ar<sub>2</sub><sup>+</sup>), which cannot be resolved using even high resolution; one of the less abundant selenium isotopes has to be chosen for analysis (e.g., <sup>82</sup>Se<sup>+</sup>). The <sup>82</sup>Se isotope can be resolved from most interferences using a resolution of 4000, but the signal cannot be resolved from <sup>82</sup>Kr<sup>+</sup>. Kr is an impurity in the argon gas. Given the surprisingly low levels of selenium present in the onions, it was not possible to obtain reliable selenium concentrations given the relatively low ion transmission and the interference from Kr.

The quantification was performed using standard addition calibration to eliminate interferences from the sample matrix. Standard addition calibration was carried out by the addition of six multielement standard solutions (Perkin-Elmer). Each standard was added at three concentration levels to separate samples. The analyses were performed in a class 1000 room (R3). One standard addition calibration curve was obtained for each element for every 20 samples of onions by assuming a similar sample solution matrix for all onion samples digested under the same conditions. The efficiency of the digestions was checked for each batch of samples (10 samples of onions from the same site) by the reference material samples in the batches.

**Soils.** The particle size distribution was determined by combined sieving and sedimentation analysis (Gee and Bauder, 1986). A 1:2.5 soil/0.01 M CaCl<sub>2</sub> suspension was used in the pH determination. Total carbon was determined by dry combustion.

**Data Processing and Statistical Analysis.** A computer program developed in Risoe's Engineering and Computer Department was capable of handling standard additions with different multielement standard solution in one procedure. The integrated data from the HR-ICP-MS instrument, dilution factors, and multielement standard concentrations were loaded into the program, and the concentrations of the elements in each sample were calculated.

The results were analyzed statistically using simple correlation coefficients (*r*) in the Statgraphics statistical software package (Statgraphics Plus, 1995).

**Cleaning Procedures.** All labware was washed with 20% citric acid, 10% nitric acid, deionized water (DW with measured resistance > 10 MΩ cm, Millipore system), and double-deionized water (DDW with resistance of 18.2 MΩ cm, Elgastat, UHQPS) and then air-dried in the clean room (R3).

The Teflon vessels were washed with 10% nitric acid, DW, and DDW between each digestion. All of the sample prepara-

**Table 4. Simple Correlation Coefficients (*r*) between Soil Properties and the Elemental Concentration (Micrograms per Kilogram) in Onion<sup>a</sup>**

element	clay/%	pH	organic C/%
Ag	0.197*	-0.126	-0.015
Al	0.373***	-0.056	-0.151
Au	0.255*	0.0871	0.275**
B	0.152	0.0102	-0.527***
Ba	0.322***	-0.099	-0.114
Be	0.097	0.392***	0.102
Bi	0.071	-0.043	0.082
Ca	0.342***	0.178	0.082
Cd	0.006	0.134	-0.055
Ce	0.328***	-0.183	-0.096
Co	0.313**	0.193	-0.314**
Cr	0.571***	0.078	-0.152
Cs	-0.055	0.766***	0.559***
Cu	0.386***	0.115	-0.152
Dy	0.142	-0.060	0.101
Er	0.056	-0.004	-0.162
Eu	0.020	0.180	-0.118
Fe	0.008	0.134	-0.381**
Ga	0.069	-0.267**	-0.023
Gd	0.214*	-0.024	0.116
Ge	-0.126	-0.017	-0.277**
Hf	-0.201	-0.409***	0.527***
Hg	0.044	-0.322**	-0.217
Ho	0.114	-0.119	-0.138
In	0.042	-0.143	0.487***
Ir	0.134	-0.113	0.142
K	0.098	0.259**	0.104
La	0.405***	-0.106	-0.084
Li	-0.305**	0.580***	0.068
Lu	0.173	0.074	0.058
Mg	-0.224*	-0.139	0.179
Mn	0.120	-0.179	-0.551**
Mo	-0.215	0.054	-0.034
Na	0.013	0.783***	-0.025
Nb	0.372***	0.079	-0.179
Nd	0.312**	-0.064	-0.006
P	0.186	0.538***	-0.174
Pb	0.418***	0.092	-0.134
Pr	0.275**	-0.155	-0.161
Pt	-0.068	-0.402***	0.542***
Rb	0.439***	-0.85	-0.144
Re	-0.220*	-0.332**	0.584***
Ru	0.081	0.507***	-0.180
S	-0.042	-0.203*	0.048
Sb	0.493***	0.315**	-0.101
Sc	0.138	-0.015	-0.125
Si	-0.078	0.433***	-0.130
Sm	0.174	0.249*	-0.157
Sn	0.577***	0.251**	-0.185
Sr	-0.175	0.044	0.354***
Tb	0.163	-0.144	0.223**
Te	0.413***	0.263*	0.067
Th	0.220*	0.180	-0.108
Ti	0.228*	0.141	0.018
Tl	-0.559***	-0.409***	0.178
Tm	0.095	0.080	0.157
U	0.161	0.293**	0.184
V	-0.076	-0.202	0.377***
W	0.685***	0.145	0.573***
Y	0.077	0.105	-0.108
Yb	0.088	0.037	0.053
Zn	0.089	-0.272**	0.539***
Zr	-0.009	-0.072	-0.034

<sup>a</sup> \*, \*\*, \*\*\*, significance at *P* < 0.05, 0.01, and 0.001 levels, respectively.

tion equipment that has been in contact with the samples was washed with DW and DDW and air-dried in the clean room (R3).

## RESULTS AND DISCUSSION

The 63 element concentrations in onion taken from 11 background areas are shown in Table 2. From the

**Table 5. Comparison of Element Concentrations (Micrograms per Kilogram of Fresh Weight): 1977–1980,<sup>a</sup> 1982–1992,<sup>b</sup> and This Study**

element	1977–1980			1982–1992				this study				
	<i>n</i>	mean	min	max	<i>n</i>	mean	min	max	<i>n</i>	mean	min	max
Pb	39	31	<30	210	43	16	<4	142	99	6.4	1.22	19.7
Cd	39	40	<9	38	43	14	<0.4	58	100	22	4.9	84
Cr					23	<16	<6	21	102	9.6	1.86	47

<sup>a</sup> Hansen and Andersen (1982). <sup>b</sup> Levnedsmiddelstyrelsen (1995).

**Table 6. Comparison of Mean Values (Micrograms per Kilogram of Fresh Weight) Reported in Various Studies and This Study**

element	Finland <sup>a</sup>	Poland <sup>b</sup>	England <sup>c</sup>	U.S.A. <sup>d</sup>	Sweden <sup>e</sup>	Netherlands <sup>f</sup>	this study
Li			45				0.64
B	2000		1400				1590
Na				23000			210000
Mg	110000			91000			100000
Al	2000		3300				250
Si	5000						11000
P	390000			280000			440000
S	460000						1230000
K	2200000			1400000			1640000
Ca	330000			270000			197000
V			3.5				0.44
Cr	10		14				9.6
Mn	2300		4100	1200			1570
Fe	4600	3200	2900	1450			2600
Co	5.0		6.0				1.84
Cu	620	400	2400	370			500
Zn	4300	3300	2700	3900	2260		3400
Rb	310		3400				380
Sr			4800				910
Mo	100		40	16			8.0
Cd	30	7.0	110	11	13	11	22
Ba			800				114
Hg	<1.0						12.5
Pb	20	59	180	5.0	20	10	6.2

<sup>a</sup> Varo et al. (1980). <sup>b</sup> Krelowska-Kulas (1993). <sup>c</sup> Ward and Savage (1994). <sup>d</sup> Wolnik et al. (1985). <sup>e</sup> Fuchs et al. (1976). <sup>f</sup> Wiersma et al. (1986).

data material outliers were omitted. For some elements it was necessary to remove one to five estimations after spiking on high levels due to tailing. Therefore, the numbers of samples (*n*) in Table 2 are different. The detection limits (micrograms per kilogram) are taken as 3 times the standard deviation of 10 replicates of the blank determination. The elemental concentrations within the sites were uniform. The mean, median, minimum, and maximum values in Table 2 are calculated from all samples from the 11 sites. For most of the elements the mean exceeds the median (Table 2) because a few sites have very high values. Some elements have concentration levels below the mean of 10 consecutive blank determination; these are listed as *b* > *c* in Table 2. In these cases the negative values (*c* – *b*) are included in the statistical calculations.

As shown in Table 2, great variation exists between minimum and maximum values. Because only one genotype of onion was grown on the range of soils, these variations are probably related to soil properties. The compositions of the soils differ greatly (Table 3). Thus, the organic carbon and clay contents range from 0.88 to 2.6% C and from 4.2 to 10.8% clay, respectively. Accordingly, the pH varies from 5.5 to 7.6. These variations in properties are considered decisive for the content and distribution of trace elements in the soil (Bibak, 1994).

The results of the correlation analysis are shown in Table 4. Simple correlations between clay contents and the concentrations of Li, Mg, Re, and Tl were significantly negative ( $P < 0.05$ ) and significantly positive ( $P$

< 0.05) with Ag, Al, Au, Ba, Ca, Ce, Co, Cr, Cu, Gd, La, Nb, Nd, Pb, Pr, Rb, Sb, Sn, Te, Th, Ti, and W (Table 4). This is in good agreement with other investigations showing the importance of clay as an elemental sink in soils and the elements' availability to plants (Bibak, 1994; Alloway, 1995). Furthermore, clay-rich soils also contain more weatherable primary minerals in the silt and sand fractions than the other soils (Møberg et al., 1988). Although the elemental concentrations are highly correlated with the clay percentage the contribution from silt- and sand-sized weatherable (primary) minerals, and hence the parent materials, certainly not to be overlooked, the clay contents as well as the elements' availability to plants depend very much on the composition of parent materials (Bibak et al., 1994). The contents of Be, Cs, K, Li, Na, P, Ru, Sb, Si, Sm, Sn, Te, and U showed positive correlation with pH. Whereas the correlations for Ga, Ge, Hf, Pt, Re, Tl, and Zn were negative (Table 4), correlations between organic carbon and the content of Au, Cs, Hf, In, Pt, Re, Sr, Tb, V, W, and Zn were positive and negative for B, Co, Fe, Ge, and Mn (Table 4). These are in good agreement with many investigations showing the importance of pH and organic matter on availability of the elements to the plants (McKenna et al., 1993; Öborn et al., 1995; Saarela, 1985; Jinadasa et al., 1997).

Table 5 compares the data for Pb, Cd, and Cr in this study with those of two other major surveys conducted in Denmark by the National Food Agency of Denmark (1977–1980 and 1988–1992). The level of Pb found in this study is lower than those previously reported. The

**Table 7. Leek In-House Check Sample from the National Food Agency of Denmark<sup>a</sup>**

element	certified	measured
Cd	0.201 ± 0.022	0.211 ± 0.022
Pb	0.75 ± 0.18	0.74 ± 0.13
Cu	4.25 ± 0.23	3.89 ± 0.19
Zn	22.4 ± 2.2	28.9 ± 5.3
Mn	12.9 ± 2.6	15.2 ± 2.3

<sup>a</sup> All concentrations given as mg/kg with the standard deviation.

higher level of Pb in the previous investigation may be an airborne contamination, in agreement with Ward and Savage (1994). They noted the potential of motor vehicle activities changing the overall magnitude of soil Pb chemistry at sites along motorways, hence increasing uptake by plants. It is generally agreed that Pb from a soil source is not readily translocated to edible portions of plants. The main process responsible for Pb accumulation in such plants is deposition of Pb directly onto leaf surface and absorption through cell walls.

Table 6 compares the data for Li, B, Na, Mg, Al, Si, P, S, K, Ca, V, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Mo, Cd, Ba, Hg, and Pb from this study with those of the other major surveys conducted in different countries or reported by other workers. The contents of B, Mg, K, Mn, Fe, Cu, Zn, Rb, Cd, and Pb are comparable to those reported previously (see references in Table 6). The contents of Na, P, S, Si, and Hg are higher and those of Li, Al, Ca, V, Cr, Co, Sr, Mo, and Ba are lower than those previously reported (Table 6). A variety of factors such as selection of fields, sample genotypes, sampling, sample handling, and analytical methods may be responsible for these differences.

As shown in Table 2, great variation exists among the sites. The concentrations of the elements may vary from sample to sample, and crop cultivars display distinct patterns of relatively wide geographical areas. However, for minor elements, the general pattern for Zn > Fe > Mn > Cu is comparable to that reported by Wolnik et al. (1985).

The elemental mean and standard deviation of 11 replicate analyses of the leek in-house check sample from the National Food Agency of Denmark are shown in Table 7 (a primary CRM for onion is not commercially available). For the five certified elements in the leek in-house sample from the National Food Agency of Denmark listed, a good order of accuracy was obtained using HR-ICP-MS. Comparison of data between the certified and measured values validates the sample digestion method used and provides a degree of confidence in the accuracy of the other element results obtained by this HR-ICP-MS analytical method.

The precision of the HR-ICP-MS method for some selected elements is shown in Table 8. All concentrations are given as the average of the measured concentrations in 10 subsamples taken from the same onion. All sample preparation procedures were performed in parallel. In general, the relative standard deviation (%RSD) of the HR-ICP-MS is <15%, when the concentration of the element considered is well above the detection limit. There are, however, a few exceptions, for example, Cr, for which the %RSD is somewhat higher (27%). This is due to the fact that even in a clean room, it is very difficult at these low concentrations to completely avoid contamination with Cr from chemicals and sample containers. The large deviation is a result of variations in the Cr background level. The same

**Table 8. Precision of the HR-ICP-MS Method**

element	concentration <sup>a</sup> (μg/kg)	%RSD
Fe	4299	8.2
B	1917	3.7
Mn	1300	6.1
Cu	603	11
Ba	425	12
Rb	291	3.4
Cr	6.4	27
Cd	6.2	11
Co	5.1	6.2
Ce	3.8	14
Tl	0.64	18
Li	0.32	44
Y	0.21	14
Pb	5.3	11
Nd	0.12	43
Pr	0.09	27
Tb	0.03	54
Dy	0.07	71
Lu	0.009	61

<sup>a</sup> Concentrations are not corrected for blank.

applies for Zn (17%RSD) and Si (27%RSD). When the concentration of an element is close to or below the detection limit, the %RSD rises, as expected: see Li, Pr, Tb, Dy, Lu, and Nd, for which the %RSD is >40% (Table 8).

The methodology used in this study can be efficiently employed to study a wide range of elements in agricultural crops. Results are important in providing nutritional information on the trace elements of onion.

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