only in minor quantities, and might not be of concern in itself.

In this study, only a few isolates of *Alternaria* were examined, and even this limited sampling found high variability in mycotoxin production between *Alternaria* strains. No attempt was made to examine all fruits and vegetables that are known to serve as hosts for *Alternaria*. Since the *Alternaria* are one of the most common organisms responsible for the spoilage of fruits and vegetables, the natural production of these mycotoxins in the food supply may constitute a potential hazard to human health.

The possibility exists that contaminated fruits may be incorporated into processed products, such as juices, preserves, and sauces, through faulty sorting procedures or neglect and thus constitute a potential health hazard. At present we are surveying some of the most common processed foods and studying the stability of the *Alternaria* mycotoxins to processing and storage conditions.

ACKNOWLEDGMENT

We thank M. J. Ceponis of the USDA Station, Rutgers University, New Brunswick, NJ, K. D. Hickey of the PSU Fruit Research Laboratory, Biglerville, PA, and J. W. Eckert of the Department of Plant Pathology, University of California, Riverside, CA, for samples of infected fruits and *Alternaria* isolates.

LITERATURE CITED

Bjeldanes, L. F.; Chang, G. W.; Thomson, S. V. *Appl. Environ. Microbiol.* **1978**, *35*, 1150.
Harvan, D. J.; Pero, R. W. *ACS Monogr.* **1976**, *No. 149*, 344.
Heisler, E. G.; Siciliano, J.; Stinson, E. E.; Osman, S. F.; Bills, D. D. *J. Chromatogr.* **1980**, *194*, 89.
Pero, R. W.; Posner, H.; Blois, M.; Harvan, D.; Spalding, J. W. *EHP, Environ. Health Perspect.* **June 1973**, 87.
Sauer, D. B.; Seitz, L. M.; Burroughs, R.; Mohr, H. E.; West, J. L.; Milleret, R. J.; Anthony, H. D. *J. Agric. Food Chem.* **1978**, *26*, 1380.
Scott, P. M.; Stoltz, D. R. *Mutat. Res.* **1980**, *78*, 33.
Steyn, P. S.; Rabie, C. J. *Phytochemistry* **1976**, *15*, 1977.
Stinson, E. E.; Osman, S. F.; Heisler, E. G.; Siciliano J.; Bills, D. D. *J. Agric. Food Chem.* **1980**, *28*, 960–963.

Received for review December 22, 1980. Accepted April 27, 1981. Reference to a brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Determination of Trace Amounts of Selenium in Corn, Lettuce, Potatoes, Soybeans, and Wheat by Hydride Generation/Condensation and Flame Atomic Absorption Spectrometry

Mark H. Hahn, Roy W. Kuennen, Joseph A. Caruso, and Fred L. Fricke*

Because of the nutritional and toxicological significance of low selenium concentrations in agricultural crops, a sensitive, accurate, and precise method for selenium analysis at part per billion levels is required. A procedure utilizing wet digestion followed by hydride generation/condensation–flame atomic absorption has been developed for the routine analysis of selenium in different varieties of soybeans, wheat, potatoes, lettuce, and sweet corn. The lowest quantifiable level, based on 2 g of sample, is 1 ng/g (dry weight) for all crop types studied. The precision for the total analysis is 3.7% relative standard deviation (RSD) at a mean concentration of 100 ng/g and 13% RSD at a mean concentration of 1 ng/g. Sample recoveries, precision studies, and analyses of NBS reference materials demonstrate the reliability and accuracy of this technique. A summary of results for 830 crop samples is reported.

The importance of trace level selenium determination in plant samples is partially a result of the discovery that selenium is not only a toxic element [LD_{50}(rat) = 300–500 μg of Se/100 g of diet] but also essential for the prevention of certain nutritional diseases among particular animal species (Schwarz and Foltz, 1957).

In the past two decades, the selenium concentration in plant material has been the subject of many studies in all parts of the world. Pasture species from Western Australia (Gardiner et al., 1962; Gardiner and Gorman, 1963), plants from all over the United States (Kubota et al., 1967), hay and forage crops from the Pacific Northwest (Carter et al., 1968), and forage crops from Canada (Walker, 1971) are a few examples of these studies.

Concern over both nutritional and toxicological effects of selenium present in human and animal diets has prompted this study to establish natural, pollution-free selenium levels in some common crop samples grown on various soil types throughout the United States.

Routine methods of selenium determination which are applicable to the analysis of plant materials include colorimetry (Gutenmann and Lisk, 1961), fluorometry (Watkinson, 1960; Allaway and Carey, 1964; Inhat, 1974), atomic fluorescence using hydride generation (Tsujii and Kuga, 1974; Thompson, 1975), flame atomic absorption using solution nebulization (Allan, 1961) and hydride generation (Manning, 1971), and flameless atomic absorption (Baird et al., 1972; Inhat and Westerby, 1974; Wauchope and McWhorter, 1977).

A high degree of accuracy and precision at very low selenium concentrations is necessary for proper assessment of nutritional and toxicological levels. The methodology

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45220 (M.H.H., R.W.K., and J.A.C.), and U.S Food and Drug Administration, Elemental Analysis Research Center, Cincinnati, Ohio 45202 (F.L.F.).

presented here has proven to be both precise and accurate, as well as procedurally routine, for trace selenium determinations in a large number of samples. Detection involves the formation and condensation of hydrogen selenide (Knudson and Christian, 1973), followed by flame atomic absorption spectrometry.

EXPERIMENTAL SECTION

Sample Collection. Samples were selected from agricultural sites chosen to represent "contamination-free" environments from major production areas. The following criteria were used as guidelines in site selection for all crops. The site was more than 1 mile (or 5 miles downwind in the prevailing wind direction) from a coal-fired power plant or similar large fossil fuel plant. A distance of at least 200 m from a U.S. or State highway (100 m from rural roads) was observed. The site was 100 m from a current, abandoned, or known building site that had been obliterated. In addition, the sampling sites were at least 50 m from end rows or other areas where large quantities of fertilizer or other materials were likely to have spilled or stockpiled during normal operations and at least 10 m from field boundaries.

Preparation of Dried Samples. Samples received from the field were washed with deionized water (18 megohm, Millipore Corp., Bedford, MA) and dried in a clean-air environment provided by vertical laminar flow hoods equipped with 0.3-μm HEPA filters (Environmental Air Control Inc., Hagerstown, MD). Any equipment contacting the samples during preparation was nonmetallic and had been scrupulously cleaned: glassware with 30% HNO_3 and plasticware with deionized water. All sample handling subsequent to the washing procedure was done in a clean-air environment, and disposable polyethylene gloves were worn throughout the procedure.

Washed samples were reduced to their edible portions and chopped into small pieces in a food chopper (Hobart Corp., Troy, OH) coated with a vinylidene fluoride resin (Pennwalt Corp., Philadelphia, PA). Those samples with high water content (corn, lettuce, and potatoes) were placed into glass freeze-dry flasks, frozen in a shell freezer at −50 °C, and freeze-dried (Labconco, Kansas City, MO). Wheat samples were soaked in deionized water overnight and freeze-dried to facilitate grinding. These dried samples, and also soybeans, were ground in a commercially manufactured blender (Sears, Roebuck and Co., Chicago, IL) to pass a 420-μm polypropylene sieve and stored in acid-washed linear polyethylene bottles. The final sample composite represented 5 heads of lettuce, 10 ears of sweet corn, soybeans from 80 pods, 10 potatoes, or (grain kernels from) 200 full heads of wheat.

Reagents. Redistilled nitric acid, ACS Reagent, and doubly distilled perchloric acid, 70% ACS Reagent (G. F. Smith Co., Columbus, OH), sulfuric acid, ACS Reagent (Mallinckrodt, McGraw Park, IL), hydrochloric acid, ACS Reagent (Fisher Scientific Co., Fair Lawn, NJ), magnesium perchlorate, ACS Reagent, calcium chloride, anhydrous, and ammonium vanadate, ACS Reagent (Matheson Coleman and Bell, Norwood, OH), and H_2, He and N_2 gas cylinders (Liquid Carbonics, Chicago, IL). An acid dilution solution was made by the addition of 200 mL of HCL and 100 mL of H_2SO_4 to make 1 L in deionized water. A 4% solution (w/v) of sodium tetrahydridoborate, 98% (Alfa-Ventron, Danvers, MA), in 10% (w/v) NaOH, ACS Reagent, was suction filtered through a medium-porosity glass filter until clear (Knechtel and Fraser, 1978). Selenium standard (10 μg/mL) was prepared by dilution of a 1000 μg/mL atomic absorption standard in 20% HCl and 10% H_2SO_4.

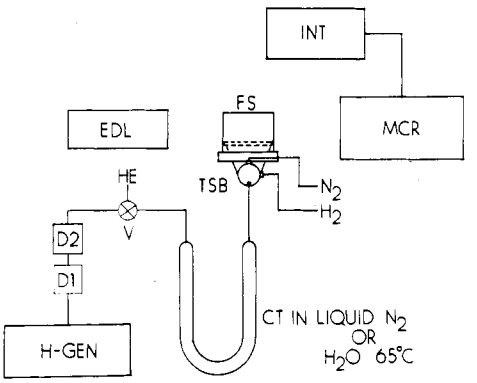

Figure 1. Hydride generation/condensation apparatus for determination of selenium. H-GEN, hydride generator; D1 and D2, desiccant tubes; V, three-way valve; CT, condensation tube; TSB, triple-slot burner; FS, flame shield; EDL, electrode-less discharge Se lamp; MCR, monochromator; INT, recording integrator.

Sample Digestion. A 2-g sample was weighed on an analytical balance and added to a 100-mL Kjeldahl flask containing 30 mL of a (3:2:1) nitric, perchloric, and sulfuric acid mixture and 0.02 g of NH_4VO_3. The flask was heated slowly on a six-unit micro-Kjeldahl digestion rack until foaming subsided and were then adjusted to constant boiling. Color change from yellow to orange to red followed the progress of the digestion from boiling nitric to perchloric to sulfuric. As the fumes of SO_3 evolved, heating was continued until the vapor ring of H_2SO_4 reached the neck of the flask. Upon completion of the digestion, ~5 mL of H_2SO_4 remained. This was cooled and quantitatively transferred with several portions of deionized water to a 50-mL volumetric flask containing 10.0 mL of concentrated HCl, and dilution to volume was made with deionized water. One reagent blank consisting of 30 mL of the acid digestion mixture with NH_4VO_3 was prepared with each 10–15 samples. Recovery of a standard amount added to a sample prior to the digestion was demonstrated every five samples, and 5% of the total number of samples prepared was determined in duplicate.

Apparatus. A schematic diagram of the generating and trapping apparatus is provided in Figure 1. Ten milliliters of the diluted digests was analyzed by hydride generation–flame atomic absorption. A pressurized reagent pumping system, controlled by an electronic timer (Fiorino et al., 1976), was used for the addition of $NaBH_4$ reducing solution.

A liquid nitrogen condensation trap was placed between the reaction tube and the flame reservoir to facilitate the separation of copious amounts of hydrogen gas produced during the reaction from the analyte. The trap consists of a 2-ft section of 0.5 in i.d. corrugated Teflon tubing (SGA Inc., Bloomfield, NJ) packed about half full with 1-mm Teflon shavings.

Analytical Determination. Flame gases were adjusted (H_2, 1875 mL/min, and N_2, 6820 mL/min) to achieve maximum response for a standard amount of Se at the analytical wavelength (196.0 nm). The condensation tube was immersed in the liquid nitrogen trap and a timer was started. A 10-mL aliquot of the sample was pipetted into the reaction tube which was attached to the reaction head of the generator. Valve I (Omnifit, Cedarhurst, NY) was adjusted so that the reaction tube was open to the condensation tube, and the flow of He carrier gas was stopped. After the condensation tube had been cooled in the liquid N_2 for 45 s, the time device on the generator was activated, and 12 mL of $NaBH_4$ solution was delivered over a 7-s interval, followed by a 5-s flush of the delivery tube with deionized water. Valve I was then adjusted to reestablish

the flow of He carrier gas through the condensation tube and to close the reaction tube to the system. The reaction tube was removed from the generator and rinsed with deionized water while residual H_2 was carried out of the condensation tube (5 s). The condensation tube was removed from the liquid N_2 and immersed in a hot water bath (65 °C). After 4 s, the integrator was started and the next sample aliquot prepared.

RESULTS AND DISCUSSION

The digestion procedure used by Fiorino et al. for the complete oxidation of NBS orchard leaves and NBS bovine liver, which utilizes 30 mL of 4:1:1 HNO_3–$HClO_4$–H_2SO_4, proved to be inadequate for the digestion of NBS wheat flour. The range of recovered Se using this procedure was 60–65% of the certified value, and the highest value recorded in over 100 digestions was 70%.

Several digestions were attempted in an effort to prevent volatilization loss of Se. These were "wet pressure" digestion with HNO_3/$HClO_4$ in sealed 4-oz Nalgene bottles (Adrian, 1971), "wet pressure" followed by digestion with 4:1:1 HNO_3–$HClO_4$–H_2SO_4, and a reflux condenser used with the HNO_3–$HClO_4$–H_2SO_4 digestion. Recoveries in the 60–65% range for all three techniques suggested that the low recoveries were not the result of volatilization losses but of incomplete hydride formation caused by the presence of unoxidized organic moieties. Further evidence of this was obtained by results from digestions that were spiked with stock solutions containing 10 μg each of Cu^{2+}, Fe^{3+}, Zn^{2+}, Ag^{2+}, Hg^{2+}, and Ti^{3+}. The first three, Cu^{2+}, Fe^{3+}, and Zn^{2+}, were added in an attempt to bind the Se in an intermetallic complex. Ag^{1+}, Hg^{2+}, and Ti^{3+} were chosen for their high formation constants with the halogens (especially Cl^- and Br^-), which are known to form volatile compounds with Se. There was no increased Se recovery in any of these cases.

Efforts to increase the efficiency of oxidation began with attempts to achieve better control and intensity of the oxidation potential of the acid mixture. To this end, the Bethge apparatus was employed. This apparatus allows the stepwise increase of the boiling perchloric acid concentration and provides control of the oxidation potential through careful monitoring of the temperature of the boiling $HClO_4$–water azeotrope (Smith, 1965). Although a small increase in Se recovery was noticed, results were still not within the acceptable range certified for NBS wheat flour.

Replacement of the 4:1:1 (HNO_3–$HClO_4$–H_2SO_4) acid mixture in the procedure used by Fiorino et al. with a 3:2:1 ratio (Gorsuch, 1959) increased the analyte recovery from NBS wheat flour to 72–75% of the certified value and proved to be markedly more consistent. This result is presumably due to the more complete oxidation of the sample matrix with thee increased $HClO_4$ concentration present in the acid digest.

The addition of milligram amounts (0.01 g/g of sample) of NH_4VO_3, as an oxidation catalyst (Smith, 1965), to the 3:2:1 acid mixture increased the Se recoveries to 85–90% of the certified amount which is on the low end of the acceptable range for NBS wheat flour. Increased amounts of NH_4VO_3 failed to enhance the oxidation further, and amounts larger than 0.05 g of NH_4VO_3/g of sample decreased the amount of selenium recovered. Therefore, the final digestion medium was composed of NH_4VO_3 (0.01 g/g of sample) and the 3:2:1 (HNO_3–$HClO_4$–H_2SO_4) acid mixture. This medium was utilized for all crop samples in this study.

When the digestion is completed, only H_2SO_4 and vanadium remain with the sample digest. It is important to note that all of the perchloric acid must be expelled from the digestion flask, as trace amounts severely hinder the repeatability of the condensation/revolatilization process. The use of 30 mL of a 3:2:1 (HNO_3–$HClO_4$–H_2SO_4) acid mixture leaves 5 ± 0.5 mL of H_2SO_4 at the end of the digestion.

With this amount of H_2SO_4, maximum sensitivity for generation of SeH_2 was found with the addition of 20% (v/v)HCl, since the SeH_2 generated in the $NaBH_4$/acid reaction is dependent on the total acid concentration. To correct for the varying H_2SO_4 concentration, we determined all samples by the method of standard additions. This method also assured that possible chemical interferents with the hydride generation (Smith, 1975) were taken into consideration in the quantification of Se in the crop samples. Initially, the addition of two standard amounts (0.1 and 0.2 μg of Se) was used, but since a one-point standard addition produced the same results in most cases, the shorter method was preferred. One-point standard addition allowed each sample to be determined in 3 min. Variation of the increase in signal, resulting from the addition of a standard amount, from a normal value was seen as a possible matrix interference, and a second standard addition was made. At this point in the study, over 800 samples have been analyzed for Se, and the increase in signal from the addition of a standard amount (0.10 μg) has shown no significant deviation in the different crop types. The fact that for over 95% of the samples determined, the increases of signal by standard addition to the sample are equal in magnitude to the change in signal from corresponding amounts of standard Se stock solution (in the same acid) illustrates that either there are not usually substantial concentrations of chemical interferents in this group of crop samples or they are eliminated by the final addition of HCl (Vijan and Leung, 1980).

Since the transient peak shapes obtained in the Se detection step depend on the reaction rate and the amount of time spent by the analyte in the cold trap, an electronic recorder–integrator (Hewlett-Packard, Palo Alto, CA) was added to integrate peak areas and, therefore, remove these factors as critical parameters of the determination.

The most significant source of day–to–day variation in response of the system to SeH_2 is a change in flow rate of either H_2 or N_2 flame gases. Small changes in gas flow (especially of the H_2) produce rather large shifts in sensitivity. A less critical factor affecting the response of the system, but one that should be mentioned, is the time that the condensation tube is cooled prior to the generation of the hydride. The time chosen (45 s) is the minimum time required to effectively trap all of the generated SeH_2. Longer precooling times, up to 90 s, result in identical integrated peak area (peak height is affected), but after 1.5 min., a noticeable decrease (10% or greater) in sensitivity is seen, probably due to decomposition in the presence of other volatile reaction products.

The physical transport of water vapor from the reaction tube into the condensation tube by the large volume of gaseous reaction products is noticeable. An accumulation of condensed water vapor in the condensation tube not only physically blocks the condensation/revolatilization of the analyte but also causes decomposition of the condensed SeH_2 analyte species. For this reason, two drying tubes are inserted between the reaction tube and the condensation tube. The first contains anhydrous $Mg(ClO_4)_2$ and the second contains anhydrous $CaCl_2$. The first drying tube must be refilled every 20–25 reactions and reconditioned with 1 or 2 reactions, and the $CaCl_2$ must be replaced about every 100 reactions. This combination

Table I. SRM Results

	Se values, μg/g		
	NBS certified value	hydride condensation[a]	hydride condensation[b]
NBS SRM 1567 (wheat flour)	1.1 ± 0.2	0.951 ± 0.043	0.901 ± 0.051
NBS SRM 1568 (rice flour)	0.4 ± 0.1	0.315 ± 0.014	
NBS SRM 1571 (orchard leaves)	0.08 ± 0.01	0.072 ± 0.007	

[a] Mean and standard deviation based on five replicate analyses of 1-g samples. [b] Mean and standard deviation based on 50 replicate analyses over 9 months.

Table II. Standard Recoveries (0.05 μg/g)

crop	no. of recoveries	mean std Se recovery, μg/g	mean % recovery
lettuce	30	0.047 ± 0.005	94.6
potatoes	30	0.048 ± 0.003	95.7
soybeans	60	0.048 ± 0.005	96.1
corn	10	0.043 ± 0.007	85.3
wheat	50	0.049 ± 0.004	97.2

of desiccants allows for the most trouble-free, long-term operation of the system of any combination tested. Others tested were combinations of calcium chloride, molecular sieve, magnesium perchlorate, sodium borohydride, sodium hydroxide, and calcium sulfate. Problems with preconditioning, hydride instability with strong bases, and the number of reactions allowed before clogging were their most typical shortcomings.

The calibration curve constructed from microliter additions of 10 μg/mL Se^{4+} stock solution to 10-mL aliquots of the dilution acid [20% HCl (v/v) and 10% H_2SO_4 (v/v)] is linear from 0.001 to 0.25 μg of Se. For samples containing greater amounts of Se, it is necessary only to decrease the amount of sample digest being analyzed from 10 mL to as little as 0.100 mL and to adjust the total volume in the reaction tube to 10 mL with the dilution acid. This effectively allows for a working range up to 25 μg without further dilution of the sample digest. The response of several different amounts of Se^{6+} stock solution was compared to response factors from a calibration curve for identical amounts of Se^{4+}. No change in SeH_2 signal was observed, possibly because of the reductive action of HCl (Vijan and Leung, 1980) in the dilution solution or because of the presence of excess $NaBH_4$.

The accuracy of the analytical method was established by determination of Se in NBS standard reference materials (SRM) and by quantitative recovery studies of submicrogram amounts of Se added to the sample in the digestion flasks before oxidation. Results of the analysis of NBS SRM 1567 (wheat flour), SRM 1568 (rice flour), and SRM 1571 (orchard leaves) are given in Table I. In all cases, the values obtained in the hydride evolution/condensation method fall within the range of the NBS certified values.

The data for the recovery studies are identified by crop type and presented in Table II. The data shown are for recovery of 0.05 μg/g of Se^{4+} standard added to the samples before digestion. Recoveries of standard amounts in the 0.01–1.00 μg/g range were also made from several samples with no difference in percentage recovered as a function of the amount of standard added. Also, recoveries of Se^{6+} standard were made from the same samples and showed comparable results.

Precision data (Table III) and a comparison of duplicates from all five crop types over a wide range of selenium concentrations (Table IV) provide a general overview of the precision that can be expected in the routine application of this analytical method.

The use of this technique for proper assessment of toxicological and nutritional levels of Se depends largely

Table III. Precision Study

sample type	mean Se content, μg	no. of replicates	% RSD
standard	0.2	10[a]	0.8
standard	0.1	10[a]	1.3
standard	0.05	10[a]	2.3
standard	0.025	10[a]	2.9
standard	0.010	10[a]	8.5
potatoes	0.270	8[b]	8.5
potatoes	0.001	6[c]	13.1
wheat	0.138	6[c]	2.7
wheat	0.096	6[c]	3.7
soybeans	0.240	6[c]	3.7
lettuce	0.053	6[c]	2.3
corn	0.108	6[c]	3.1

[a] Replicate analyses of the stock solution. [b] Replicate analyses spanning 8 weeks. [c] Replicate analyses of sample composite through the entire method.

Table IV. Precision of Duplicates

sample Se content, μg	no. of duplicates[a]	range of % deviation[b]	av % deviation
0.015-0.050	7	6.6-16.0	14.4
0.050-0.500	15	2.0-9.0	6.7
0.500-1.35	6	2.0-11.1	3.1
0.015-1.35	28	2.0-16.0	6.8

[a] Number of samples determined in separate duplicate analysis. [b] % deviation = 100 × [(difference of Se content of duplicate analysis)/(mean Se content)].

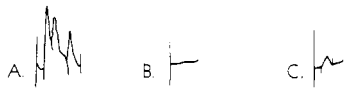

Figure 2. Effect of H_2 blank removal. Response at 196.0 nm. (A) Response from reagent blank as H_2 generated in the $NaBH_4$ reaction passes through the flame. (B) Response from the same reagent blank after separation and removal of H_2 using the condensation trap. (C) Response from 0.01 μg of Se standard after separation and removal of H_2 using the condensation trap.

on the use of the liquid nitrogen condensation trap. The ability to separate H_2 gas from analyte allows for complete elimination of the relatively large blank signal caused by increased H_2 in flame. The response in Figure 2A is the recorder signal resulting from the increased absorption of the incident radiation as the excess H_2, generated in the $NaBH_4$/acid reaction of the reagent blank, passes through the flame. Figure 2B is the recorder response from the same reagent blank after separation (and removal) of the H_2 using the condensation trap. Figure 2C shows the response from a sample aliquot containing 0.01 μg of Se, likewise separated from the H_2 absorption. The elimination of the absorption by generated H_2 from analyte absorption clearly allows for much improved detection limits and better precision and accuracy at low selenium concentrations. Because there is virtually no background signal to be considered (Figure 2B), the normal definition

Table V. Homogeneity Study

sample identifn	selenium content, μg: 2-g sample	1-g sample	% deviation[a]
soybeans no. 1	0.260	0.245	5.9
soybeans no. 2	0.028	0.033	16.1
soybeans no. 3	0.564	0.587	3.9
soybeans no. 4	0.081	0.074	9.0
soybeans no. 5	0.025	0.019	27.2
wheat no. 1	0.159	0.144	9.9
wheat no. 2	0.354	0.324	8.8
wheat no. 3	0.778	0.789	1.1
wheat no. 4	0.280	0.305	8.5
wheat no. 5	0.432	0.453	4.7

[a] % deviation = [(difference in Se content between a 1- and 2-g sample determination)/(average Se content)] × 100.

Table VI

state	no. of samples	range of Se dry wt, μg/g	av Se, μg/g
	Corn		
Florida	45	ND[a]	ND
California	15	0.075-0.208	0.136
totals	60	ND-0.208	0.068
	Lettuce		
Arizona	15	0.008-0.130	0.029
California	40	ND-0.274	0.084
Florida	30	ND-0.215	0.023
Texas	40	0.010-0.115	0.038
totals	125	ND-0.274	0.048
	Potatoes		
Alabama	30	0.005-0.103	0.025
Idaho	25	ND-0.010	0.004
Maine	30	ND-0.010	0.001
New York	10	ND	ND
Texas	25	0.038-0.144	0.073
Washington	30	ND-0.299	0.019
totals	150	ND-0.299	0.022
	Wheat		
Kansas	45	0.020-0.512	0.202
Montana	30	0.114-3.12	0.960
Nebraska	45	0.065-0.434	0.221
North Dakota	25	0.169-2.26	0.777
South Dakota	15	0.244-1.34	0.646
Texas	30	0.065-0.871	0.328
totals	190	0.020-3.12	0.457
	Soybeans		
Arkansas	30	0.040-0.958	0.265
Illinois	35	0.018-1.09	0.092
Indiana	45	0.013-0.298	0.046
Iowa	50	0.012-0.583	0.176
Louisiana	50	0.019-1.62	0.457
Minnesota	50	0.061-2.23	0.354
North Carolina	45	ND-0.149	0.058
totals	305	ND-2.23	0.213

[a] ND = not detectable.

of detection limit as twice the standard deviation of the background (blank) signal does not provide the means for its calculation. The limit of quantitation of Se in this case is the ability of the integrator to recognize and integrate the Se absorption peak with some degree of reproducibility. With a reported RSD of 13% at a mean Se concentration of 1 ng/g, we are justified in reporting a lowest quantifiable level of 1 ng/g (dry weight) based on the digestion of a 2-g sample. In the case of wheat and soybean samples, which often contain higher Se concentrations, it is possible to digest 1 g of the sample using only 15 mL of the (3:2:1) HNO_3–$HClO_4$–H_2SO_4 acid mixture. In addition to a 50% savings in amount of acid needed, the time for completion of the digestion is also cut in half.

The data in Table V for 1-g vs. 2-g samples compare within experimental error to the data established in Table V for duplicate analyses of 2-g samples. This favorable comparison between 1- and 2-g samples indicates a high degree of homogeneity in the preparation of the sample from the raw agricultural crop. Table VI represents the results for 830 samples, part of a continuing comprehensive survey on background Se levels for various crops collected from their growing sites throughout the United States. No conclusions will be drawn from the data reported here since these results represent only a preliminary portion of the total sampling and analyses.

ACKNOWLEDGMENT

This work was conducted in cooperation with the U.S. Department of Agriculture Soil Conservation Service and U.S. Environmental Protection Agency in conjunction with Memorandum of Understanding No. 224-79-2462.

LITERATURE CITED

Adrian, W. J. *At. Absorpt. Newsl.* **1971**, *10*, 96.
Allan, J. E. *Spectrochim. Acta* **1961**, *18*, 259.
Allaway, W. H.; Carey, E. E. *Anal. Chem.* **1964**, *36*, 1359.
Baird, R. B.; Pourian, S.; Gabrielian, S. M. *Anal. Chem.* **1972**, *44*, 1887.
Carter, D. L.; Brown, M. J.; Allaway, W. M.; Carey, E. E. *Agron. J.* **1968**, *60*, 532.
Fiorino, J. A.; Jones, J. W.; Capar, S. G. *Anal. Chem.* **1976**, *48*, 120.
Gardiner, M. R.; Armstrong, J.; Fels, H.; Glencross, R. N. *Aust. J. Exp. Agric. Anim. Husb.* **1962**, *2*, 261.
Gardiner, M. R.; Gorman, R. C. *Aust. J. Exp. Agric. Anim. Husb.* **1963**, *3*, 284.
Gorsuch, T. T. *Analyst (London)* **1959**, *84*, 150.
Gutenmann, W. H.; Lisk, D. J. *J. Agric. Food Chem.* **1961**, *9*, 488.
Inhat, M. *J. Assoc. Off. Anal. Chem.* **1974**, *57*, 368.
Inhat, M.; Westerby, R. J. *Anal. Lett.* **1974**, *7*, 257.
Knechtel, J. R.; Fraser, J. L. *Analyst* **1978**, *103*, 104.
Knudson, E. J.; Christian, G. D. *Anal. Lett.* **1973**, *6*, 1039.
Kubota, J.; Allaway, W. H.; Carter, D. L.; Cary, E. E.; Lazar, V. A. *J. Agric. Food Chem.* **1967**, *15*, 448.
Manning, D. C. *At. Absorpt. Newsl.* **1971**, *10*, 123.
Schwarz, K.; Foltz, C. M. *J. Am. Chem. Soc.* **1957**, *79*, 3292.
Smith, A. E. *Analyst (London)* **1975**, *100*, 300.
Smith, G. F. "The Wet Chemical Oxidation of Organic Compounds"; G. F. Smith Chemical Co., Inc.: Columbus, OH, 1965.
Thompson, K. C. *Analyst (London)* **1975**, *100*, 307
Tsujii, K.; Kuga, K. *Anal. Chim. Acta* **1974**, *72*, 85.
Vijan, P. N.; Leung, D. *Anal. Chim. Acta* **1980**, *120*, 141–146.
Walker, D. R. *Can. J. Soil Sci.* **1971**, *51*, 561.
Watkinson, J. H. *Anal. Chem.* **1960**, *32*, 981–983.
Wauchope, R. D.; McWhorter, C. G. *Bull. Environ. Contam. Toxicol.* **1977**, *17*, 165.

Received for review October 9, 1980. Accepted February 23, 1981.