1.0 ppm just before death or at the last sampling period. The residues of cadmium in the urine of control sheep were generally <0.01 ppm, but occasionally levels of >0.03 were found.

The pretreatment level of cadmium in the wool of both treated and control sheep was <1.0 ppm. The level of cadmium increased in the control sheep as well as in the treated sheep. The greatest residue of cadmium in the wool of the treated sheep was >20.0 ppm and in the control sheep was >10.0 ppm. Again the residues were inconsistent. Because the wool samples were washed and dried before analysis, the external contamination of the wool due to dirt, feces, urine, and other contaminants should have been eliminated. Possibly the cadmium from the external contamination absorbed into the hair of the control sheep.

The residues of cadmium found in the tissues and bone of sheep are summarized in Table IV. Residues were greatest in the liver and kidney of the treated sheep. At the lower dosages of 50 and 100 ppm, the residues of cadmium were greater in kidney than in liver, whereas, at the higher dosages (300 and 500 ppm), the residues in the liver were much greater. This difference may be due to renal damage that resulted in poorer excretion of cadmium and greater deposition in the liver. Increased BUN's at the end of the study in the sheep given the greatest dosages indicate possible kidney damage. Of the other tissues, heart had the greatest residues followed by muscle, brain, and bone. Liver and kidney of control animals had residues of >2.0 ppm. Liver and kidney samples of three lambs born during the study to ewes no. 1, 3, and 9 were analyzed. The lamb from no. 1 had no detectable residues. The lamb from no. 3 had residues of 1.3 ppm in the liver and 2.0 ppm in the kidney. The lamb from no. 9 had no detectable residues in the kidney but had 1.0 ppm in the liver. As mentioned earlier, residues of cadmium can cross the placental barrier from mother to fetus if doses are high (Friberg et al., 1971).

This research has shown that residues of cadmium will accumulate in tissues of both cattle and sheep given a cadmium fungicide in their feed. Cadmium fed at dietary concentrations of greater than 200 ppm causes possible kidney damage as indicated by the increase in BUN levels. The placenta, which serves as a barrier to low doses of cadmium, can be overcome with high doses of cadmium, and residues of cadmium will appear in the tissues of fetuses.

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Received for review June 25, 1976. Accepted November 29, 1976. This paper reflects the results of research only. Mention of a pesticide or a proprietary product in this paper does not constitute a recommendation or an endorsement of this product by the U.S. Department of Agriculture.

Vanadium Content of Selected Foods as Determined by Flameless Atomic Absorption Spectroscopy

Duane R. Myron, Samuel H. Givand, and Forrest H. Nielsen*

The vanadium contents of seven classes of foodstuffs were determined by atomic absorption spectrometry by use of a graphite furnace atomizer with deuterium arc background correction. Beverages, fats and oils, and fresh fruits and vegetables contained the least vanadium, ranging from <1 to 5 ng/g. Whole grains, seafood, meats, and dairy products were generally within a range of 5 to 30 ng/g. Prepared foods ranged from 11 to 93 ng/g while dill seed and black pepper contained 431 and 987 ng/g, respectively.

Studies by four laboratories have provided evidence that vanadium is an essential nutrient for both mammals and birds (Hopkins and Mohr, 1971; Schwarz and Milne, 1971; Strasia, 1971; Nielsen and Ollerich, 1973). The probability that vanadium is also essential in human nutrition has renewed interest in the dietary availability of this element. Information is scarce on the vanadium content of foodstuffs. For evaluation of vanadium nutriture, such information would be required, and a single reliable method for determining vanadium in a wide variety of foodstuffs would be a critical prerequisite.

United States Department of Agriculture, Agricultural Research Service, Human Nutrition Laboratory (F.H.N), and Department of Biochemistry, University of North Dakota, Grand Forks, North Dakota 58201.

Vanadium qualifies as a "micro" trace element in that it is present in biological specimens at a range from less than 1 to several ng/g (Bertrand, 1941; Schroeder et al., 1963; Söremark, 1967; Christian, 1971; Welch and Allaway, 1972). Thus, a sensitive method is necessary. The wide range of vanadium contents reported for similar materials (e.g., the colorimetric procedure of Schroeder et al. (1963) compared to the neutron activation method of Söremark (1967)) emphasizes the need for a precise and accurate method of analysis.

Atomic absorbance spectroscopy, with the flameless graphite furnace technique, provides an increase in sensitivity of approximately three orders of magnitude compared to conventional flame methods for vanadium. The benefits of the graphite furnace also include a potential for the elimination of interfering substances through selective atomization. This technique is particularly

applicable to vanadium because of its high refractivity. Deuterium arc background correction further improves selectivity by eliminating the remaining effects of nonspecific absorbing substances. Analysis for vanadium by graphite furnace atomic absorption has been reported for several types of substances (Omang, 1971; Segar and Gilio, 1973; Chakrabarti and Hall, 1973; Schramel, 1973; Muzzarelli and Roccetti, 1974). The effectiveness of the deuterium arc in correcting for interferences has been reported (Quickert et al., 1974). However, no method employing atomic absorption with deuterium arc background correction has been reported for vanadium analysis in foods. Therefore, we have examined the reliability of this method and used it for the analysis of a variety of foodstuffs.

METHODS AND MATERIALS

Reagents and Standards. Water was glass distilled prior to ultrafiltration and ion exchange treatment (Super Q System, Millipore Corp.). An Ultra Pure grade of nitric acid (Ultrex, J. T. Baker Chemical Co.) was used throughout. A 4 N solution of nitric acid prepared from these reagents contained <0.06 ng/ml vanadium. Reference standards were vanadium pentoxide (Fisher Chemical Co.) and bis(1-phenyl-1,3-butanediono)oxovanadium (National Bureau of Standards). Food materials were purchased locally and analyzed immediately.

Ashing Procedure. A char-ashing procedure was used for all samples. All substances were handled similarly except that fresh fruits and vegetables were scrubbed and rinsed with water prior to weighing. Duplicate samples (5–20 g), except for fruits and vegetables, were weighed as purchased into platinum crucibles, charred, or evaporated to dryness on a hot plate and ashed at 450 °C for 16 h in a muffle furnace. Two milliliters of nitric acid (concentrated) was added. The samples were warmed on a hot plate to dryness and ashed again at 450 °C for 2 h. The residue was dissolved in 2 ml of 4 N nitric acid, then gently warmed, and quantitatively transferred to 5-ml volumetric flasks.

Atomic Absorption Methodology. Vanadium was detected by its absorbance at 318 nm with an atomic absorption spectrometer (Model 503, Perkin-Elmer Corp.) equipped with a graphite furnace atomizer (Model HGA 2100, Perkin-Elmer Corp.). The sample volume was 50 μl. The graphite furnace atomizer was programmed for the following cycle: drying, 125 °C for 1 min; charring, 1400 °C for 1 min; atomization, 2750 °C for 15 s. The system was purged with argon at 100 ml/min. Simultaneous deuterium arc background correction was employed throughout. Absorption was monitored with a strip chart recorder (Model 56, Perkin-Elmer Corp.). The relation between absorbance and vanadium content was linear from 0 to 10 ng. Detection limit was approximately 0.3 ng, and a "memory effect" was observed above 5 ng. Thus, the optimal range of vanadium content was from 2 to 5 ng.

RESULTS AND DISCUSSION

Recovery Studies. Vanadium is known to possess several oxidation states, and may complex with a variety of ligands including some macromolecules (Vallee and Wacker, 1970). Since these factors might vary from one food to another, the recovery of vanadium, in two different forms, from reference material was determined. Vanadium(IV) as bis(1-phenyl-1,3-butanediono)oxovanadium and vanadium(V) as vanadium pentoxide were added, respectively, to lyophilized rat liver and lyophilized bovine liver prior to ashing. The data from Table I show that both forms of vanadium were recovered equally well (from 89 to 92%). It should be noted, however, that successful recoveries alone do not necessarily constitute a proof of reliability for this method. Bovine liver (National Bureau of Standards Reference Material 1577) contained 55 ± 2 ng of vanadium/g. Rat liver, from a pool of rats fed laboratory chow, contained 8 ± 2 ng/g. Standard orchard leaves (National Bureau of Standards Reference Material 1571) contained 370 ± 11 ng of vanadium/g, which approximates the 361 ± 9 ng/g for identical material analyzed by Welch and Cary (1975) with a catalytic method. The National Bureau of Standards did not report a vanadium content for either reference material.

Table I. Content and Recovery of Vanadium in Standard Materials

	V added, ng	V found, ng	Recovery, %
Bovine liver,[a] 3.0 g	0	166 ± 2	
	200[d]	350 ± 7	92
Rat liver,[b] 3.0 g	0	24 ± 2	
	200[e]	202 ± 6	89
Orchard leaves,[c] 1.0 g	0	370 ± 11	

[a] National Bureau of Standards Reference Material 1577. [b] From pool of lyophilized and pulverized rat livers. [c] National Bureau of Standards Reference Material 1571. [d] As V_2O_5. [e] As bis(1-phenyl-1,3-butanediono)-oxovanadium(IV).

Analysis of Foodstuffs. The selected food materials that were analyzed for their vanadium contents are listed in Table II. Vanadium content varied considerably between the groups of foods.

The vanadium content of cereals and grains is generally higher than that of fresh fruits and vegetables. This difference may be due in part to the high water content of fresh fruits and vegetables. Processed or prepared foods contained the most vanadium. Breads, breakfast cereals, and the gluten fraction of wheat contained several times the vanadium content of the grain itself. Furthermore, white rice (polished) contained much more vanadium than brown rice. Although the variation from geochemical factors cannot be ruled out, significant quantities of vanadium apparently are introduced by mechanical means during the processing of foods. The introduction of a significant quantity of vanadium into plant material by passage through a brass sieve has been demonstrated (Welch and Allaway, 1972).

Of foods tested, the seeds of dill and black pepper, the only spices examined, contained the most vanadium, 431 and 987 ng/g, respectively. Although the dietary intakes of these spices per se may be small, they might contribute significantly to the vanadium content of some prepared foods.

With the exception of chicken, fresh meats contained from 1 to 6 ng of vanadium/g (Table II). The light or breast meat of chicken (22 ng/g) contained the same amount of vanadium as egg yolk, but almost twice as much as dark meat (12 ng/g). Seafoods appear to be a better source of vanadium than red meats, approximating the level found in chicken breast meat.

Milk appears to be a significant dietary source of vanadium, but a fivefold variation in the vanadium content of milk, depending on geographic location, has been described (Söremark, 1967). Apparently, the vanadium in milk is water soluble, since it is relatively more abundant in skim milk than in butter.

Drinking water and beverages, except beer, appear to contribute very little to the total dietary intake of vanadium. However, beer would constitute a major dietary source of vanadium for a large portion of the population

Table II. Vanadium Content of Foodstuffs

	V, ng/g		V, ng/g
Cereals, grains, and seeds		Beverages	
Hard spring wheat[a]	3	Water[a]	1.8
Durum wheat[a]	6	Coffee	1.6
Barley[a]	14	Tea	1.3
Navy beans	14	Cola, canned	0.7
Field peas	7	Beer, canned	11
Brown rice	<1	Fresh fruits and vegetables	
White rice	21	Potato[a]	<1
Oatmeal	6	Cabbage	2
Gluten	33	Carrot[a]	1
Corn meal	2	Lettuce	4
Dill seed	431	Cauliflower	<1
Black pepper	987	Squash[a]	4
Meats and dairy products		Radish	5
Beef liver	6	Tomato[a]	2
Pork chop	1	Banana	3
Chicken (dark)	12	Apple	4
Chicken (light)	22	Oil and fats	
Ground beef	1	Margarine	4
Bacon	5	Butter[a]	1
Bologna	8	Corn oil (supermarket)	1
Milk, whole[a]	3	Lard, commercial	2
Milk, skim, powder	25	Soybean oil	1
Egg yolk[a]	21	Prepared foods	
Seafood		Dill pickles	13
Codfish	28	Peanut butter	44
Scallops	22	Milk shake, chocolate	21
Lobster	5	Breakfast cereal, natural	93
Tuna (canned)	11	White bread[a]	20
		Whole wheat bread[a]	11

[a] Produced in the locality of Grand Forks, N.D.

if the beer we analyzed is representative.

The vanadium content of the fats and oils tested ranged from 1 to 4 ng/g and no distinct difference was apparent between plant and animal sources. These vanadium levels are strikingly less than those reported by Welch and Cary (1975) for a variety of vegetable oils. However, the methods of digestion and analysis used by Welch and Cary (1975) differ considerably from those reported here. Considerable variation may be expected among commercial oils since processing often involves the removal of trace metals to prevent autoxidation and flavor changes (Beal and Sohns, 1971).

Among the foods and dietary ingredients we examined for vanadium, most fell within a range from 1 to 30 ng/g, fresh weight. Of the few reports relating to vanadium content of foods, our values agree most closely with those of Söremark (1967) who used a neutron activation method for analysis of vanadium. The eight items which were commonly analyzed include drinking water, milk, potatoes, apples, tomatoes, lettuce, carrots, and dill. Our range of 3 to 14 ng/g for cereal grains is in agreement with the values reported by Welch and Cary (1975) using a catalytic method. However, Schroeder et al. (1963), who used a colorimetric method, reported values averaging >1000 ng/g for 25 different fresh vegetables and 21 grains and cereals. Materials of local origin are indicated in Table II. The vanadium content of plant-derived material may reflect geochemical factors such as type and vanadium concentration of soil (Welch and Cary, 1975). Söremark (1967) has reported a tenfold variation in vanadium content of drinking water from different worldwide locations. Tissues of rats fed a vanadium-deficient diet contain significantly less ($p < 0.001$) vanadium than those fed an adequate diet (Myron et al., 1975), suggesting that the vanadium content of animal tissues should be higher in vanadium-rich geographic areas than in vanadium-poor regions. Thus, geographic origin may significantly influence the vanadium content of plant and animal material.

We made no attempt to estimate an average daily intake for vanadium as a more thorough and comprehensive study of dietary vanadium exposure must be undertaken. Factors including organocomplex formation and valence state must be considered in determining the bioavailability of vanadium from foods. It is apparent that most processed and prepared foods are relatively rich in vanadium. Thus, the average intake of vanadium may be increasing as more processed foods are being consumed.

ACKNOWLEDGMENT

The authors wish to thank Mike Collings for expert technical assistance.

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Received for review October 4, 1976. Accepted November 29, 1976. This study was supported in part by United States Public Health Service Grant No. HL 19530 and the United States Department of Agriculture Cooperative Agreement No. 12-14-100-11, 178 (61), Amendment 1. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable.

Control of Chromium Concentrations in Food Plants. 1. Absorption and Translocation of Chromium by Plants

Earle E. Cary,* W. H. Allaway, and Oscar E. Olson[1]

Plants accumulated Cr from nutrient solutions but retained most of this Cr in the roots. The barrier to translocation of Cr from roots to tops of plants was not circumvented by supplying ^{51}Cr in the form of organic acid complexes, Cr(III), Cr(VI), or by increasing the Cr(III) concentration in the nutrient solutions. Plants, or plant tissues, that tend to accumulate Fe also accumulate Cr. Attempts to increase the Cr concentration in certain leafy vegetables seem more promising than attempts to increase Cr in edible seed crops. Chromium concentration in some leafy vegetables grown with a continued supply of soluble Cr may be tenfold greater than those found in surveys of Cr in foods.

The primary objective of this series of experiments was to provide a basis for designing crop production practices that might increase the chromium (Cr) concentration in food and feed crops. Mertz et al. (1974) discussed the potential value of an increase in levels of dietary Cr in a nutritionally effective form. Mertz (1969) outlined some of the chemical properties of Cr that may affect the role of this element in biological systems.

Much early (Pratt, 1966) and recent (Turner and Rust, 1971) work on Cr in plants was concerned with Cr toxicity. All of this work indicates that Cr(VI) is more toxic to plants than Cr(III) and that plants showing visual symptoms of toxicity contain very little more Cr in their tops than did normal plants. Although there are reports of plant growth responses to addition of small amounts of Cr to soils or culture solutions, recent experiments using highly purified cultures and sensitive analytical techniques indicate that if Cr is essential to the tested species, the required levels (in terms of concentration in plant tissue) are lower than for any known essential nutrient (Huffman and Allaway, 1973a).

Lyon et al. (1969a), who studied the metabolism of Cr in the accumulator plant *Leptospermum scoparium*, found Cr trioxalate to be one of the Cr compounds present in roots and leaves. In another study, this group (Lyon et al., 1969b) found CrO_4^{2-} in extruded xylem sap of *L. scoparium* when $Na_2{}^{51}CrO_4$ was fed to the roots. However, chromate was not found in soluble fractions of leaves, stems, and roots.

Myttenaere and Mousny (1974) reported evidence of greater removal of Cr(III) and Cr(VI) than of CrEDTA from nutrient solutions by rice roots, but a higher percentage of the Cr from CrEDTA taken up by the roots was translocated to the rice tops than was the case for Cr(III) or Cr(VI). The chemical form of Cr in the roots, as measured by solubility in different extractants, seemed similar regardless of whether Cr(III) or Cr(VI) was added to the nutrient solution.

Huffman and Allaway (1973b) found that over 90% of the ^{51}Cr removed from solutions by beans and wheat was still in the roots 20 days after the last addition of ^{51}Cr to the solutions. Most of this Cr was in soluble fractions. Less than 0.1% of the total ^{51}Cr in the plant was in the seeds. The ^{51}Cr in the leaves was primarily in the form of a low molecular weight anionic complex.

Shewry and Peterson (1974) intensively studied the uptake and translocation of CrO_4^{2-} from nutrient solutions by barley seedlings. They suggest that most of the Cr retained in the roots is present in soluble form in vacuoles of root cells. Very little translocation of Cr from the roots to the tops took place except at concentrations of CrO_4^{2-} in the solution high enough to injure the roots.

EXPERIMENTAL SECTION

General Methods. Seeds were germinated in sand and grown with one-half strength Johnson's (Johnson et al., 1957) solution containing FeEDTA. Individual plants were then removed from the sand, the roots were washed, and the plants were placed in polystyrene holders so that the roots were suspended in continuously aerated treatment solution.

Reagent grade chemicals were used and ^{51}Cr was carrier free. Concentrations of stable Cr were determined by the method of Cary and Olson (1975) and ^{51}Cr activity was measured using γ-ray spectrometry (Nuclear-Chicago automatic γ well counting system). A large sample volume detector (Nuclear-Chicago, Tobor) was used for ^{51}Cr activity measurements of roots or tops from entire plants.

Organic Cr complexes were prepared by reacting ^{51}Cr(III) with the ligands at 80 °C for 20 h at a Cr:ligand ratio of 1:3. Cr(III) and Cr(VI) were verified by paper electrophoresis.

Uptake and Translocation of Different Forms of Cr by Various Plant Species. The objective of this group of exploratory experiments was to rapidly survey various crops and different sources of Cr to identify potential opportunities to increase the Cr concentration in the tops of edible plants.

Wheat (*Triticum aestivum* C.V. Chris), corn (*Zea mays*

U.S. Plant, Soil and Nutrition Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Ithaca, New York 14853.

[1]Present address: Station Biochemistry, South Dakota State University, Brookings, S.D. 57006.