

Rapid Determination of Selenium in Foodstuffs by Neutron Activation Analysis

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방사화분석법에 의한 식품중의 Se의 정량

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Abstract

The selenium content of a wide variety of Korean food was determined by neutron activation analysis. Most fruits and vegetables contained quantities of selenium less than $0.4 \mu\text{g/g}$. Grain products varied widely in their selenium content with $0.5 \mu\text{g/g}$ and barley cereal as high as $0.7 \mu\text{g/g}$. Dried milk powder sample ranged from 0.07 to $0.15 \mu\text{g/g}$. Chicken muscle contained about $0.7 \mu\text{g/g}$. The content of sea food was generally higher, ranging from 0.3 to $3.65 \mu\text{g/g}$. These values suggest that a diet well balanced in other nutrients is probably also nutritionally adequate with regard to selenium, although possible effects of cooking and biological availability remain to be investigated.

Introduction

Many biological and analytical investigations have been carried out to determine the toxic properties of selenium.⁽¹⁻³⁾ Selenium toxicity has been associated with its presence in drugs, detergents⁽⁴⁾, moistening agents⁽⁵⁾, coal, oil, gas⁽⁶⁾ etc. and measures to control its presence has become necessary. Introduced as sodium selenite into the tissues of greenhouse plants, its toxicity protects against attack by insects, as an internal insecticide⁽⁷⁻⁸⁾. The effect of the selenium in cattle fed with grass grown in soils that contain selenium are widely known. Its toxicity has been recognized the poisonous material in certain accumulator plants growing in areas where soils contain selenium; these plants cause blind

staggers and alkali disease in cattle eating them.⁽⁹⁾ The carcinogenicity of seleniferous wheat fed to rats was described in 1943 by Nelson and his colleagues.⁽¹⁰⁾ Selenium was first discovered to be an element essential for mammals and birds by Schwarz⁽¹¹⁻¹³⁾ who found that traces would prevent dietary liver necrosis in rats⁽¹⁴⁻¹⁵⁾ and exudative diathesis in chicks.⁽¹⁶⁻¹⁸⁾ In this respect, relatively large doses produce hepatic necrosis. Selenium salts, however, usually can be replaced in deficient animals by vitamin E.⁽¹⁹⁾ To studying life-term effects of selenite and selenate in rats for subclinical toxicity, we have surveyed human foods and tissues for concentration of selenium. In spite of this overwhelming body of evidence strongly implicating selenium as a nessential trace element for all

species, there have been few data to suggest the occurrence of a selenium deficiency in man. Although the selenium content of wide variety of animal feeds has been surveyed in the literature,⁽²¹⁾ there exist few data concerning amounts of selenium in food consumed by humans. Recently a considerable therapeutic success with dietary supplements of selenium salt was reported⁽²⁰⁾ by the case of dietetic and liver necrosis in pig⁽²¹⁻²²⁾. The distribution of selenium in tissues and organs of various plant species has implications in relation to both physiology and animal husbandry. Following the discovery of the biological importance of trace amounts of selenium, now nearly ten years ago, considerable effort has been devoted to the development of method for determining selenium in biological materials in amounts of less than a microgram.⁽²³⁻²⁶⁾ The determination by chemical or spectrometric method offers many difficulties.⁽²⁷⁻³⁰⁾ Available three alternative methods are activation to 120 day ⁷⁵Se used to determine⁽³¹⁻³⁷⁾ selenium in cereal diets⁽³⁸⁻⁴⁰⁾ is a slow process. Activation to 19 min ⁸¹Se (a pure beta emitter) needs fast radiochemistry and has been employed to determine selenium in plant materials.⁽⁴¹⁻⁴²⁾ Lastly activation to 18 sec ^{77m}Se precludes radiochemistry and requires a gamma spectrometer with good resolution⁽⁴³⁻⁴⁶⁾. Three of the radioactive isotopes of selenium (⁷⁵Se, ^{77m}Se and ⁸¹Se) can be produced in high specific activities of which the most desirable one ^{77m}Se has an exceedingly short half life. Nevertheless certain workers have employed selenium determination. The present paper reports values for selenium in a variety of common food items assayed using a neutron activation analysis.

Experimental Methods

1. Samples

Foods representing the Korean diet were chosen for analysis. Rice samples were Paldal and Honam species. Samples were purchased in Seoul, and Suwon area from local food stores. Gross green, milk, meat, egg, chicken, sea foods and various grain are obtained from commercial market in Seoul and other country. Sample investigations were undertaken in four regions purchased from different growing site in the period of March to November 1970.

2. Preparation of samples

A new container was opened for each analysis and duplicate aliquots taken for analysis. Fresh vegetables and fruits were homogenized in a glass food blender to obtain homogeneous samples. Only edible portions were used with the peeling being discarded in most cases. All samples were assayed as received with no cooking or drying performed, since selenium might be lost as a result of these processes.

3. Preparation of samples for irradiation

A polyethylene vial, which can be tightly stoppered, was filled with 1 ml of liquid sample. One gram each of sample was sealed in a small polyethylene vial, 1 × 2.5 cm in diameter for solid samples.

4. Standard

Selenium standard was prepared from the solution of sodium selenite (1 μg Se/ml). Sodium selenite solution was diluted using micro pipettes and volumetric flask to yield standard solution containing 0.1~20 μg Se/ml. Several series of selenium standards were prepared for irradiation by pipetting quantities of the standard solution into polyethylene vial. Each series of standards contained the same quantity of selenium capsule, but varying amount of water. The calibration for the neutron shielding effect in sample and in standard comparing the selenium standards with the same sample matrix, contained 1 μg of selenium as sodium selenite.

5. Irradiation

The sample was put into a polyethylene vial together with standard. Solution vials in a large vessel were subjected to irradiation. The irradiations were carried out in the pneumatic rabbit system of Triga-Mark II Reactor at a thermal neutron flux of about $3.8 \times 10^{12} \text{ n/cm}^2/\text{sec}$. The optimal time was 0.3 min. for irradiation.

6. Measuring procedure

Errors due to variations in time and neutron flux are compensated by using detectors to reduce the high-energy background above the selenium line. Time necessary for preparation of vial is 0.3 min, for irradiation is 0.2 min, for handling is 0.2 min, for cooling is 0.3 min, for life-time measuring is 0.3 min, and finally 0.2 min, is for spectra subtraction. In some spectra, especially for the plant materials a second γ -line of 0.20 MeV was detected, probably due to ¹⁸O-activity.

7. Counting conditions and radioactivity measurement

To eliminate the critical influence of the short half-

life each sample was not only irradiated together with a standard, but also measured with selenium standard using a multichannel analyzer.

Table 1. Nuclear data for thermal neutron activation of selenium

Target nuclide	Abundance(%)	Isotope activation cross-section (b)	Product on thermal neutron irradiation	Radiation and energy (MeV)	Half-life
⁷⁴ Se	0.87	26±6	⁷⁵ Se	EC: r 0.265, 0.136, 0.280-0.402	121 d
⁷⁶ Se	9.02	7±3	^{77m} Se	IT e^- r 0.162(Q _{IT})	17.5 sec
⁷⁸ Se	23.52		^{79m} Se	IT 0.096(Q _{IT})	3.91 min
⁸⁰ Se	49.82	0.03±0.01	^{81m} Se	IT $e^-(r)$ 0.103(Q)	56.8 min
		0.5±0.1	⁸¹ Se	β^- 1.38(Q)	18.2 min
⁸² Se	9.19	0.050±0.025	⁸³ Se	β^- 3.4; r 1.01, 2.02, 0.65, 0.35	70.0 sec
			⁸³ Se	β^- 1.5; r 0.35(both ⁸³ Se radionuclides decay independently to yield ⁸³ Br, T _{1/2} 2.3hr)	25 min

Table 2. Comparison between several methods of selenium trace analyses

Method	Practical limit of sensitivity (μ g)	Estimated speed of analysis (samples/day)	Remark	Reference
1. Spectrophotometry	0.05	20	Loss of volatile Se possible contamination of reagent	(52)
2. Fluorometry	0.02	20	" "	(53)
3. Flame Photometry	0.06	15	" "	(53)
4. Fluorescence	0.01	10	" "	(54)
5. X-ray Fluorescence	10.0	10	" "	(55)
6. Polarography	0.2	10	" "	(56)
7. Spark-Source Mass Spectrometry	0.1	10	Mineralization of the samples with the disadvantage of escape of volatile Se	(57)
8. Emission Spectrography a-c Arc Method	1.0	10	" "	(58)
9. Atom Absorption Spectrophotometry	0.1	10	" "	(59)
10. Radioactive tracer ⁷⁵ Se	0.04	35	Radiochemical separation biological disadvantages: 2 month cooling time	(21)
11. Activation analysis by ⁷⁵ Se	0.1	30	Necessary 5 day irradiation	(24)
12. Activation analysis by ⁸¹ Se	0.1	40	GM counting possible radiochemical separation	(42)
13. Activation analysis by ^{77m} Se	0.07	200	No Radiochemical separation: 3 sec irradiation and cooling	(43)

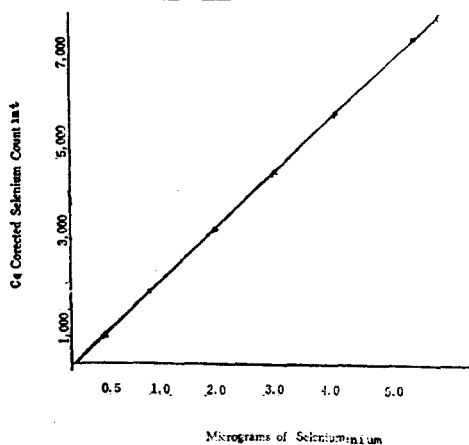
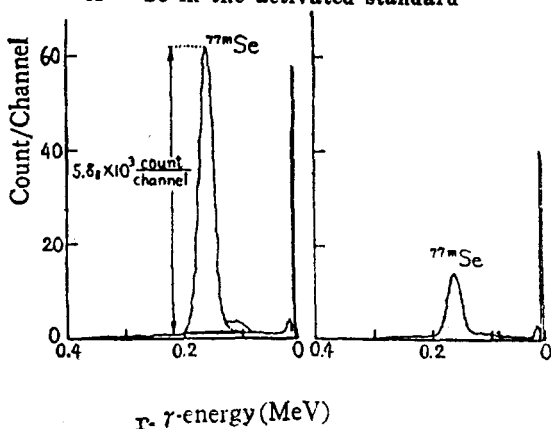
Results

It is estimated the limit of sensitivity of the analysis for selenium in one gram sample to be 0.25 μ g. Each sample was irradiated twice and the mean was calculated. Although the sensitivity of these analyses was estimated

to be 10⁻² ppm of selenium, the reproducibility of results was only \pm 10 per cent on amounts of the order of a few μ g (Fig. 1,2). Radioactivities of selenium in the standard in the same experimental conditions are given in Table 3. It appears, that these results are in good agreement with the data,

Table 3. Results from analysis of selenium ^{77m}Se standard

Amount of Se(μg)	Radioactivity (cpm)
0.25	422
0.5	887
1.0	1,803
2.5	3,658
5.0	7,520
10.0	15,170

**Fig. 1. Calibration curve for gamma-ray spectra of ^{77m}Se in the activated standard****Fig. 2. Gamma-ray spectra of ^{77m}Se in different conditions.**

	A	B
Activation time	18(sec)	18(sec)
Wait time	15(sec)	55(sec)
Count time	20(sec)	20(sec)
Live time	30(sec)	30(sec)

The selenium value for grain products assayed are given in Table 4. Grain products varied greatly in their selenium contents. The amount of selenium is around 0.4 ppm in Paldal, which is higher value than

Table 4. Selenium content in Korean grains and cereal products

Product	Se content in wet state (μg)	Se content in dry state (μg)
Rice (edible), Paldal	0.37	0.90~1.47
Rice (edible), Honam	0.28	0.25~1.75
Unpolished rice	0.50~2.60	0.58~3.04
Barley (local)	0.77	0.84
Barley	0.34	0.42
Soy-bean	0.7~0.75	0.85~1.51
Wheat	0.4~1.10	0.43~1.28
Flour		0.52
First clear flour		0.43
Low grade flour		0.52

that in the rice of Honam district produced. Generally, the amount of selenium is two times more than the unpolished. The contents of selenium is also varied in flour; the lowest grade showed 0.09 ppm more than the highest grade. It is also varied in grain produced from different area owing probably to the difference of soil composition. Generally, home-produced grain has less content of selenium comparing the American produced. Most vegetables were found to contain less than 1.0 μg Se/gram as shown in Table 5. Cabbage contained 0.88 $\mu\text{g}/\text{g}$; radish 0.25 $\mu\text{g}/\text{g}$; and carrots 0.82 $\mu\text{g}/\text{g}$. In cabbage and cucumbers, the selenium contents is 2~5 times more than in the other vegetables. Furthermore, the selenium contents in home-produced vegetables is much less comparing the values estimated by Hamilton⁽⁷⁶⁾, for crop, plant, and vegetables produced in America.

Table 5. Selenium content in Korean vegetables

Product	Se content in dry state ($\mu\text{g}/\text{g}$)
Spinach	0.25
Egg plant	0.42
Cabbage	0.88
Cucumber	0.57
Carrot	0.82
Radish	0.25
Kale	0.26
Potato	0.18
Potato peels	0.09
Turnips	0.38
Lettuce	0.02
Squash	0.07

Table 6. Selenium content in Korean Fruits

Product	Se content in dry state ($\mu\text{g/g}$)
Apple	0.03~0.48
Orange	0.21~0.38
Pear	0.088
Peach	0.061
Mellowed persimmon	0.12~0.42
Grape	0.031
Tomato	0.07
Apricot	0.22
Mandarin orange	0.36
Chinese date	0.42
Pine-nuts	0.48
Chestnuts	0.31

The selenium content is 0.30~0.88 $\mu\text{g/g}$ for home-produced fresh fruit and 2~3 times more for wet fruits. It is also generally less value in home-produced fruits comparing the foreign produced, except in apple.

Table 7. Content of selenium in animal feeding-stuffs

Sample	Se content on a dry basis (mg/kg)
Red clover	0.06
Ladino clover	0.25
Sweet clover	0.86
Acacia	0.14
Lespedeza	0.40
Alfalfa	0.02~0.23

It is confirmed⁽¹⁾ that the content of selenium directly influences to the disease of animal. Especially, on the results of investigation on the contents of selenium for some foodstuffs such as milk, beef, and egg in view of the influence of feeding, it is confirmed that⁽²⁾ the contents of selenium is 0.06~0.86 mg/kg of dried feed such as dried grass. It is already reported that the selenium contents in dried grass is variable depending upon the soil composition which directly influences the selenium contents in grass. Even if the plant is growing in the same area, the contents of selenium is varied from plant to plant owing to the difference of selenium stocking ratio in plant. However, in all cases, seeds contained more than 10 ppm and, therefore, could be considered as potentially toxic to livestock. These plants will only grow on seleniferous soils, and can accumulate large of selenium, up to 1 per cent dry weight. Most crop plants, grains and

grasses can accumulate up to 3 ppm, depending on the amounts of selenium in the top soil⁽³⁾

Table 8. Selenium content of miscellaneous products

Product	Wet basis $\mu\text{g/g}$	Dry basis $\mu\text{g/g}$
Milk	0.07	0.15
Margarine butter	0.09	0.135
Meat	0.71	2.25
Egg		
Yolk	0.198	0.274
White	0.038	0.045
Chicken meat	0.05	0.12

There was also variation in the selenium of the milk products assayed (Table 8). Dry milk contained 0.15 $\mu\text{g/g}$, while milk had 0.07 $\mu\text{g/g}$. Fresh meats and sea food (Table 9) were found to be very good sources of selenium. Chicken had the least selenium (0.12 $\mu\text{g/g}$) and meat, the highest (0.10~0.274 $\mu\text{g/g}$). Egg yolk as shown in Table 8 had selenium values three times higher than egg white (0.038~0.045 $\mu\text{g/g}$). The contents of selenium in milk is 0.15 ppm for home-produced but 0.11 ppm for American produced. However, the content is 0.21 ppm less for home-produced egg and chicken meat than the American produced. According to these data, we can estimate that the selenium content is appropriate in Korean livestock.

Table 9. Selenium content in Korean sea-foods

Sample	ppm
Undaria pinnatifide	0.41
Dried laver	0.24
Anchovy brand A	1.54
Anchovy brand B	1.30
Anchovy brand C	0.94
Anchovy brand D	2.30
Yellow-corvina	3.25
Dried yellow corvina	3.62
Hair tail	2.25
Eel	2.65
Shrimp (deveined)	0.84
Sea-ear	1.75
Cuttle fish	1.85
Oysters	0.37
Shrimp	1.47

Sea foods (Table 9) were found to be very good source of selenium. The average content of sea foods

(0.42-3.62 $\mu\text{g/g}$) was considerably higher than that of meat (0.27 $\mu\text{g/g}$). It is estimated that the content in small anchovy is 1.20 ppm more than that in the big one. For yellow-corvina, we obtained the largest value, 3.60 ppm. For shell fish species, it was 1.50 ppm which is unexpected large value. Shell fish such as oysters shrimp had an average selenium content of 0.84 $\mu\text{g/g}$. There is no difference in content of selenium between the eel growing in sea-water and the eel growing in the river. Sample could be analyzed for selenium in manner which did not require chemical separation after irradiation. Analysis of identical sample dried for prolonged periods of time showed that no selenium was lost by volatilization during drying. The selenium contents in a number of common goods, are shown in Table 4~9. Three of the four locally grown grains, however, lacked this element. There was little selenium in vegetables and fruits. Selenium content was 0.07~1.57 ppm for 11 sample of vegetables. Selenium is known to be volatile and it has been reported by Fink⁽¹⁴⁾ that the selenium content of skimmed milk powder was variable according to the method of drying. The effects of processing and cooking upon the selenium content of foods need to be known so that we may calculate the amounts of selenium consumed by the human being. Some foods, which has been heated in processing, had low concentrations (0.37 $\mu\text{g/g}$) where as raw grains in general contained more selenium (0.23 $\mu\text{g/g}$). Selenium in foods is probably quite volatile and may be largely lost in cooking. In sample cooked daily eats containing meats and seafood, egg, mean concentration was only 0.08 $\mu\text{g/g}$, where as the raw sea foods, and meat had 1.4 $\mu\text{g/g}$.

Discussion

A problem existing in trace-element studies is the necessity of a higher sensitivity of the analytical method than in the detection of poisoning. In the case of selenium the sensitivity must be better by 10 times since the nutritive and toxic level of selenium lie close together. We could not find a particularly rapid method of selenium determination. Selenium measurements have also been reported⁽⁶⁰⁾ by forensic scientists interested in the origin of samples of opium, they analyzed for selenium⁽⁶¹⁾. The use of $^{77\text{m}}\text{Se}$ for deter-

mining selenium by neutron activation analysis was described in 1960 for the first time⁽⁴⁸⁾. Table 1 summarizes the nuclear characteristics of selenium relevant to activation with thermal neutron^(45,60) and the nuclear reaction occurring upon bombardment of selenium with thermal neutrons. The nuclides of a comparable half-life are also very rare in biological materials where little interfering radioactivity was produced. If selenium is bombred with thermal neutrons⁽⁶²⁾, $^{80}\text{Br}(n,p)$ is radioactive and could lead to $^{77\text{m}}\text{Se}$ only through a secondary reaction of low probability. $^{80}\text{Kr}(n,\gamma)$ $^{77\text{m}}\text{Se}$ has little biological material but the cross-section for (n,γ) reaction with nuclears in this mass region are very small. Care must also be taken to obtain the exact time at which counts are recorded for rapidly decaying nucleares. The calibration for absolute selenium amount was carried out by comparing the pure selenium standard with another standard having to some matrix and geometry as the samples.

Table 10. Possible, radionuclides having gamma energy of more than. 0.16MeV(62)

Nuclide formed	Half-life	Nuclide formed	Half-life
$^{183\text{m}}\text{W}$	5.5 sec	^{233}Th	22 min
$^{*77\text{m}}\text{Se}$	17.5 sec	^{181}Te	25 min
$^{77\text{m}}\text{Ge}$	54 sec	^{123}Sn	40 min
$^{185\text{m}}\text{Dy}$	1.25 sec	$^{111\text{m}}\text{Gd}$	49 min
$^{185\text{m}}\text{W}$	1.62 min	^{136}Ba	84 min
^{171}Gd	3.6 min	^{177}Yb	1.9 hr
$^{182\text{m}}\text{Ta}$	16.5 min	$^{85\text{m}}\text{Kr}$	4.4 hr
^{70}Ga	21 min	^{188}Re	17 hr

* Show similar shape of γ -spectra.

Table 11. Short half lived γ radionuclide ($T=10^1-10^2\text{sec}$)formed by neutron irradiation (Not contained the nuclide of which cross section is too small)

Nuclide	Half-life	γ -energy (MeV)
$^{167\text{m}}\text{Er}$	2.5 sec	0.208
$^{178\text{m}}\text{Hf}$	4.8 sec	0.427
$^{70,80}\text{Er}$	5.0 sec	0.21
$^{183\text{m}}\text{W}$	5.5 sec	0.155, 0.105
^{20}F	10.7 sec	1.63
$^{77\text{m}}\text{Se}$	17.5 sec	0.162
$^{179\text{m}}\text{Hf}$	19 sec	0.215, 0.160

^{46m} Sc	19.5 sec	0.142
¹¹⁰ Ag	24.2 sec	0.66, 0.94, 0.88, 0.81
¹⁰⁴ Rh	44 sec	0.556, 1.24
^{76m} Ge	48 sec	0.139
^{165m} Dy	1.25 min	0.52, 0.36, 0.16, 0.108
¹⁹² Ir	1.42 min	0.0580
^{185m} W	1.62 min	0.165, 0.130
²⁸ Al	2.27 min	1.78
¹⁰⁸ Ag	2.3 min	0.63, 0.60, 0.43

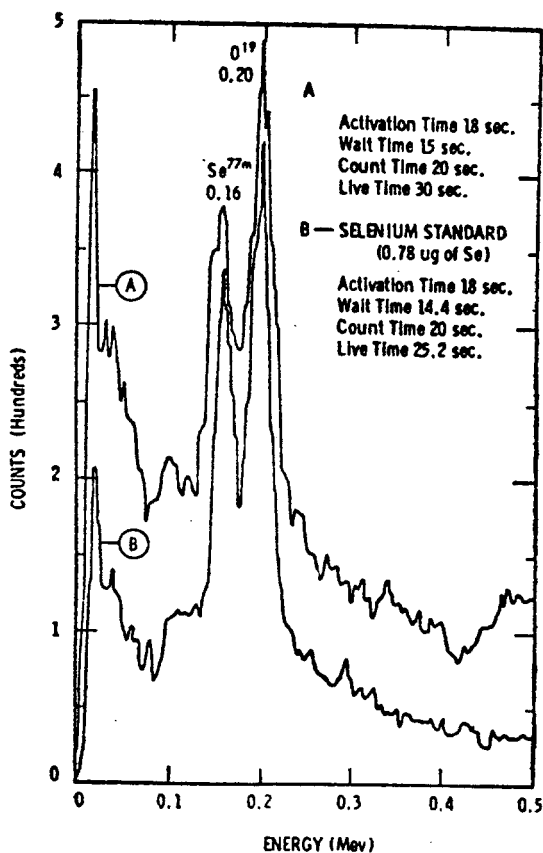


Fig. 3. Gamma-ray spectra of ^{77m}Se in the activated plant sample compared with that of selenium standard

If samples are very much, larger quantities of selenium is to produce they suggested,⁽⁶³⁾ appreciable amounts of volatile selenium compounds. The very short half-life of ^{77m}Se (17.5 seconds) means, generally, that only automatic measurements by gamma-spectrometry are possible. McConnell⁽⁴⁷⁾ found, for the most part, good agreement between methods utilizing ^{77m}Se.

Present evidence would favor the measurement of radioactive selenium in non-destructive methods by ^{77m}Se rather than ⁷⁵Se, on the counts of both rapidity and sensitivity. However, the sensitivity by gamma-counting the 0.16 MeV specific activity of the gamma-ray is about 90% internally converted. The short half-life and high activation cross-section made possible a high sensitivity even with very short irradiation times (3 sec). Problems arising from the matrix activity (mainly ²⁴Na) are minimized and a chemical separation is unnecessary. In some spectra, especially for the plant materials a second γ -line of 0.20 MeV was detected, probably due to a ¹⁹O-activity. This nuclide is formed by (n, γ) reaction with an isotopic cross-section of 4×10^{-7} b and a half-life of 29 sec.⁽⁶⁰⁾ In such cases the 0.20 MeV peak was subtracted by graphical spectra extrapolation and comparison with initial selenium-free standard spectra of same plant material. Another correction procedure for ¹⁹O interference has been described in the recent article by Dickson⁽⁴⁵⁾. The over-all sensitivity of the method was estimated as 0.1 μ g within an accuracy of $\pm 10\%$.

Belonging to Group VI A of the periodic table, it lies below sulfur and is found in association with sulfides, as is tellurium. Selenium in soil solutions, according to Bowen⁽⁶⁸⁾, ranges in concentration from 0.0001~3 ppm, and in dry soils 0.01~2 ppm, mean 0.2 ppm. River water contains less than 0.2 ppm, providing less than 70×10^6 kg added to the ocean annually. Concentrations in melted snow and rain varied from 0.06~1.40 μ g/l. It is previously reported that the activation analysis technique is the most precise means for the determination of trace element in the grain as well as for the determination of selenium in feed-grass and in fertilizer. Komiya⁽⁶⁴⁾ has determined the selenium contents in cigarettes and has determined the trace elements in tea. Takeo⁽⁶⁵⁾ and Filby⁽⁶⁶⁾ have quantitatively analyzed the selenium content in the crystalline lens, by non-destructive method, and Lambert⁽⁶⁷⁾ has determined selenium content also by non-destructive method in rat to which sufficient amount of selenium was injected to bring about chronic toxicity for rat. In the activation analysis for the sample of biological tissue, it is evident the presence of ²⁴Na or ⁴²K strongly interferes the analytical process. Therefore such

interfering element should be removed first of all. It is important to study on the automation of chemical treatment and rapid systematical separation because it well contribute to the non-destructive method for activation analysis.

Considering the widely separated sources of foods today, it is unlikely that human deficiency exists. Underwood⁽¹⁾ states that there are three groups of diseases; those caused by vitamin E deficiency alone (encephalomalacia in chicks), those due to deficiency of vitamin E and selenium, (exudative diathesis in birds, and muscular dystrophy in several species, all of which are controlled by either selenium or vitamin E) and those due to selenium deficiency alone (such a retarded growth and infertility of rats). Most of these diseases respond to selenium administration. Therefore selenium in small amounts is concerned with normal growth and function of muscle and liver and with fertility. High levels of sulfate can increase deficiency by interfering with selenium. Experimental deficiency produces necrosis of the liver in rats deficient in vitamin E, and muscular dystrophy in mouse^(1,3). High levels of unsaturated fatty acids in the diet aggravate the deficiency. The requirement of soluble selenium for rats may be less than 0.7 μg per day⁽⁶⁸⁾, in our experience it is less than 0.05 ppm in food.

In man, symptoms and signs reported include discolored chronic arthritis, of hair and nails. In Oregon, Hadimarkos⁽⁴⁰⁾ has found a relation between selenium intake of school children and dental caries. Over human toxicity has occurred only in persons living in seleniferous areas and consuming local food. Experimental selenosis is associated with necrosis of the liver. Retention of organic selenium in tissues is greater than that of inorganic forms. Selenium toxicity, from whatever source, produces loss of fertility, defects in the eyes. It is interesting that both deficiency and toxicity of selenium causes retarded growth, muscular weakness, infertility and focal necrosis of the liver. We have found that selenite in drinking water is extremely toxic to rats at 3 ppm selenium, whereas selenate is not⁽⁶⁹⁾. Further studies have indicated relatively high serum cholesterol levels in rats given selenate and selenite⁽⁷⁰⁾, with a considerable increase in aortic lipids. In mice, selenite was toxic to females

but not to males, where as selenate was not toxic at all. Because of the extremely small requirement one can calculate the toxicity as 100~300 times the required dose. Nelson⁽¹⁰⁾ reported that rats fed selenium in the form of seleniferous grain or as a mixed selenite developed liver tumors. These observations have been supported by a more recent study of Tschertes⁽⁷³⁾ who was able to induce the formation of liver tumors in rats by feeding selenium as sodium selenate. Whether selenium should be classified as a carcinogen on the basis of these reports is moot point.

Clayton⁽⁷¹⁾ alternately fed 5 ppm sodium selenite and an azo dye carcinogen to rats, and found about half as many tumors developing in the selenium fed as in the dye-fed animals. Therefore, it appears that under certain circumstances of diet and perhaps environment, selenium induces malignant tumors, and that under other circumstances, especially when life span is short, it does not. It also appears that some compounds of selenium may inhibit growth of malignant tumors in the rat and mouse. The situation may be analagous to that of radiation, by which tumors can be both induced and treated. Industrial selenium toxicity has been recognized since 1917; it is fully discussed by Browning.⁽⁷²⁾ She lists no recorded cases of malignant disease which could be attributed to toxic exposures. From these date and those of Howell⁽⁷⁵⁾, we can calculate the approximate intake and excretion of selenium. Howell⁽⁷⁵⁾ calculate the average intake at 150 μg per day from values in the literature. Although the minimal human requirement, if any, is not known, that of the rat is less than 0.05 ppm in food, and may be 0.02~0.01 ppm, a considerable number of foods in Table 4~9 show this concentration or more. The present results suggest that the level of selenium in the Korean diet is sufficient for good nutrition. Thompson⁽⁷⁷⁾ have shown that 0.04 to 0.10 ppm selenium are needed in the diet to prevent selenium deficiency in chickens depending on the vitamin E content of the diet.

There was little selenium in vegetable volatile. Milk analyzed at 0.096 $\mu\text{g}/\text{g}$ which is identical to the value reported by Hoffman.⁽⁷⁸⁾ The other sample contained 0.240 $\mu\text{g}/\text{g}$. This could be due to differences in the geographical origin of the samples. Environmental

factors, which have been reviewed extensively⁽³⁾ may cause the selenium concentrations in foods from different geographical areas to vary widely. The most important factor is the selenium content of the soil. Although Oregon is supposed to be one of the selenium-deficient areas as defined by Allaway⁽⁷⁹⁾, Hadjimarinos⁽⁴⁰⁾ found the difference between two samples of eggs and milk from two areas within the state to be tenfold. However, other factors could influence the amount of selenium in milk powder. For example, Fink⁽⁴¹⁾ reported that the selenium content of skim milk powder was variable according to the method of drying. This is due to the volatilization of the selenium during the drying process. Therefore, both the effects of processing and geographical location must be considered. While this work was in progress, a report concerning the levels of selenium in foods appeared in Germany,⁽⁸²⁾ the results generally agree well with our data when expressed on an equivalent basis. Little is known regarding the availability and biopotency of selenium as it occurs naturally in foods. It must be recognized that many selenium compounds are quite volatile and could thus be lost as a result of food cooking or processing. There is an obvious need for more research concerning the chemical form of selenium that occur in foods, the biological effectiveness of these various forms, and the possible effect of cooking and processing on these forms. No greater than normal concentration of residual selenium in the meats eaten by human beings could be required. The use of selenium as an additive to all feeds is hardly justifiable. In order to obtain data on environmental sources and human exposures to selenium, a trace element essential for mammals, a number of common foods, were analyzed by neutron activation analysis technique. The calculated human intake from air containing a mean of $0.001 \mu\text{g}/\text{m}^3$ was $0.02 \mu\text{g}/\text{day}$; this amount is a negligible increment of the daily intake in foods. Selenium was found in few vegetables, but sea-food, meat and most grains contained appreciable amounts. The daily intake in a standard diet was $62 \mu\text{g}$. Cooked and processed foods contained considerably less selenium than raw foods. Under some conditions, selenium is carcinogenic in rats. No recorded case of human or animals cancer is known which could be attributed to

environmental selenium, or the lack of it. This element, however, is the most toxic element we have studied.

요 약

Se은 비타민 E의 기능과 비슷한 기능을 가지고 있으므로 필수원소로 생각되나, 허용량을 조금만 넘으면 중독증을 일으키는 유해원소이다. 이러한 Se분석은 종래 방법은 시료분해중 Se의 증발로 인한 손실과 시약의 오염으로 오는 오차로 미량 분석이 힘들었다. 그러나 Se 분석을 ^{75}Se (반감기 18초)의 핵종을 이용하여 비파괴 분석으로 간편하고 고감도로 미량을 신속하게 방사화 분석을 이용하여 분석할 수가 있다.

본 실험은 한국산 곡류, 야채, 과일, 견초, 육류, 해산물 등을 분석한 결과를 외국산 것과 비교한 결과를 발표한다.

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