Determination of Germanium in Some Plants and Animals

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Z. Naturforsch. **45c**, 1250–1251 (1990); received January 9, 1989/August 22, 1990

Germanium Determination, Hydride Generation, Inductively Coupled Plasma, Emission Spectrometry, Medicinal Plant

The Ge contents of plants and animals were investigated by a wet ashing procedure by hydride generation and inductively coupled plasma atomic emission spectrometry with flow injection. The analytical results obtained indicated that Ge contents widely vary in plant and animal kingdoms in the range of 8–203 ppb.

The role of Ge in biological processes is quite extensive, as it is an essential trace element. The occurrence of Ge in biomaterials is usually in the range of 0.1 to 1.0 ppm [1]. On the other hand, it has been reported that some medicinal plants contain large amounts of Ge, *e.g.* about 185 ppm for *Zingibera rhizoma* [2]. Studies indicated that rice tends to concentrate Ge in its shoots, and phytotoxic effects were observed [3]. Ge not only inhibited seed germination in certain strains of lettuce but also retarded seedling growth in several other plants [4].

Ge in biological materials is most often determined by one of two analytical methods: (1) spectrophotometry with phenylfluorone as color forming agent [5], (2) graphite furnance atomic absorption spectrometry (GFAAS) [6]. The method of Leek and Camphell [5] with phenylfluorone has such low sensitivity (detection limit, 0.5 ppm) that the values must be considered as unreliable. Dittrich *et al.* [7] demonstrated GFAAS for the determination of μg levels of Ge. The present paper deals with the determination of Ge in plants and animals by means of a very sensitive procedure *e.g.*, hydride generation and inductively coupled plasma atomic emission spectrometry (HGICPAES) [8] coupled flow injection. Of the methods tested, wet digestion with H_3PO_4 and HNO_3 proved fastest, safest, and most efficient [9]. One gram of dried samples (dried 80 °C for 12 h) was weighed into a 100 ml tall beaker. After adding 30 ml of nitric acid and 1 ml of phosphoric acid, the samples were heated at 80 °C for 1 h covering with watch glass and allowed to stand overnight. After the predigestion, the samples were boiled at 200 °C until the dark HNO_3 fumes had subsided. The resulting sample solution was concentrated to about 1–2 ml by evaporation and then analyzed by FIAHG and ICPAES. The standard conditions for FI and the instrumental conditions for ICPAES are summarized as follows: FI – $NaBH_4$ (5% m/V in 0.25% NaOH solution), buffer (Na_2PO_4–H_3PO_4, 0.5 M, pH 6.5), ICPAES – R.f. power (1.5 kW), outer gas (12 dm^3 min^{-1}), intermediate gas (1.0 dm^3 min^{-1}), carrier gas (0.3 $dm^3 min^{-1}$), observation height (9 mm), wavelength (265.18 nm). As the method provides an absolute determination of Ge it has to be adjusted so that this amount falls into useful range of detection from about 1 ng to 10^5 ng. The Ge is determined in an aqueous matrix at the part per trillion level by a combination of HG and ICPAES. The recovery of Ge was more than 95% even when 0.05 μg of Ge was added. The detection limit for Ge was 0.5 ppb (S/N = 3), which is 20 times lower to that of HG flame atomic absorption spectrometry. Standard deviation for a 10 ng/cm^3 sample was 4% for 10 consecutive measurement. The plant and animal materials examined were collected in Hiroshima Prefecture in July 1987 except for the genera *Miscanthus, Solidago, Artemisia, Oenothera, Polygonum, Chenopodium,* and coal which were collected in Fukuoka Prefecture. 48 biological samples (plants and animals) were analyzed by this procedure. The results obtained are listed in Table I. Both plants and animals contained Ge at a ppb level. Park [4] reported the presence of Ge in the medicinal plant of a ppm level by means of flameless atomic absorption spectrometry. On the other hand, Shimomura [5] reported the presence of trace Ge lower than 3.7 ppb in the medicinal plants by atomic absorption spectrometry with electronthermal atomization. The present results show that medicinal plants contained only low amounts of Ge (12 to 37 ppb) and comparable with other plants. It was found that there is no relationship between their pharmacological effects

Reprint requests to Dr. N. Hayashi.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/90/1100–1250 $ 01.30/0

Table I. Ge contents of the plants and animals.

	Ge content [ppb] in dry weight
Seed plant	
Pinus densiflora (leaf)	23
Chamaecyparis obtusa (twig)	23
Miscanthus sinensis	20–55
Pleioblastus variegatus	33
Phyllostachys niger	22
Solidago virga-aurea (leaf)	11–14
Solidago virga-aurea (root)	31–42
Artemisia princeps	49
Aralia cordata	11
Eurya japonica (twig)	20
Chenopodium album	24
Polygonum longisetum	44
Rumex japonicus	8
Rumex acetosa	13
Oenothera erythrosepala (stem)	n.d.
Vicia angustifolia	8
Heterotropa takaoi	30
Saxifraga stolonifera	22
Pteridophytes	
Pteridium aquilinum	n.d.
Equisetum arvense	20
Lycopodium clavatum	27
Osmunda japonica	20
Bryophytes	
Neckeropsis nitidula	66
Hypnum plumaeforme	105
Rhacomitrium canescens	203
Thuidium kanedae	88
Chiloscyhus polyanthus	36
Fungi	
Canoderma applanatum	26
Microporus flabelliformis	15
Coriolus versicolor	17
Cryptoporus volvatus	n.d.
Lichen	
Parmeia tinctorum	38
Usnea diffracta	22
Algae	
Ulva fasciata	n.d.
Cladophora densa	62
Medicinal plant	
Parantica japonica	14
Houttuynia herna	20
Swertia japonica	37
Lycii fructus	13
Japanese geranium herb	13
Trapa japonica	17
Animal	
Graptosaltria nigrofuscata	16
Cryptotympana japonensis	12
Parantica sita	20
Rat (internal organs)	22
Domestic fowl (Gizzard)	10
Scomber scombus	19
Short-necked clam	18
Soil, coal and sea water	
Soil	11–29
Coal	1150
Sea water	n.d.

n.d., not detected.

and the content of Ge in the medicinal plant. As various plants absorb Ge from soil, we examined Ge contents of soil to clarify the relationship between Ge contents of the soil and Ge contents of the plants. It was found that Ge contents of the plants did not depend upon that of the soil. All of the animals examined contained Ge in the range of 11 to 22 ppb. The sea water contained no detectable Ge in ppb level, while the coal concentrated Ge up to 1150 ppb. The largest value of Ge contents in all the plants and animals was 203 ppb in the case of *Rhacomitrium canescens*. From these data, we assumed that Ge contents varies very widely in the plants and animal kingdoms in ppb level.

Acknowledgements

Grateful thanks are due to Prof. Kumamaru and Dr. Yamamoto (Department of Chemistry, Faculty of Science, Hiroshima University) for providing facilities of ICP and valuable suggestions.

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Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Allgäuer Zeitungsverlag GmbH, Kempten