Neutron Activation Analysis of Arsenic in the Dental Hard Tissues of Arsenic-devitalized Teeth

by

Eiko SAIRENJI,* Yukimichi URATA,* Motoki YAMADA,*
Toshinori SUZUKI* and Emiko SASAKI*

Introduction

It is well-known that arsenic, which migrated into the hard tissues of teeth from the arsenic devitalizing paste applied to a tooth, remains in that place for a fairly long period of time after the pulp extirpation of the said tooth. But so far little is known regarding the amount of arsenic remaining in the dental tissue and its period of duration because of difficulties in the determination of trace quantities of arsenic by the routine quantitative method. Only OTANI [1] had reported that the arsenic contents of a tooth previously devitalized with dental arsenic paste are much larger than those of a normal tooth, based on the Sandel's quantitative method of arsenic.

Neutron activation analysis is a well established procedure that is of use in the quantitative chemical determination, being particularly useful in connection with the determination of smaller quantities than has been possible by conventional methods.

Arsenic is one of the elements to which the application of neutron activation analysis is easily made [2] and, for this reason, various studies have been undertaken on the arsenic contents in biological samples by means of this method [3], [4], [5], [6]. The possible application of neutron activation analysis procedure to the determination of arsenic in human tooth has been described by GÖTTE [7] and by the present authors [8].

The present study gives the results of the neutron activation analysis of arsenic in the dental hard tissues which had been previously exposed to the dental arsenic paste for pulp-devitalization.

The Principles of Neutron Activation

When a nuclide, mass number A and atomic number Z , is bombarded with thermal neutrons, a neutron-gamma reaction ${}_Z^A\text{N} + {}_0^1\text{n} \longrightarrow {}_Z^{A+1}\text{N} + \gamma$ takes place. If the resultant nuclide (${}_Z^{A+1}\text{N}$) is unstable or radioactive, it can be identified and quantified with its characteristic emissions and half-life. Thus it is possible to calculate the amount of an

* 西連寺 永康, 浦田 行道, 山田 元樹, 鈴木 智哲, 佐々木 恵美子: *Radioisotope Research Lab., Nihon Univ. School of Dentistry.*

Part of the present paper was read before the 26th meeting of Dental Society of Nihon University, February, 1959.

element originally present. Two different methods of activation analysis are available :

A) Absolute calculation may be used with the following relationship :

$$W = \frac{M \cdot A}{(6.02 \times 10^{23}) (f) (\sigma_{AC}) (\theta) \left(1 - e^{-\frac{0.693}{T} t}\right) \left(e^{-\frac{0.693}{T} d}\right)}$$

Where

W is the weight of the considered element (grams)

M is the atomic weight of the element activated

θ is the percentage abundance of the particular isotope of the element under consideration

σ_{AC} is the activation cross section (barn = 10^{-24} cm^2)

f is the neutron flux (neutrons/cm²/sec.)

A is the induced radioactivity in disintegration per second

T is the half-life of induced radioactive isotope

t is the time of irradiation

d is the time from the cessation of the irradiation to the activity counting

(*T*, *t* and *d* are expressed in the same units.)

While, theoretically, the amount of an element can be determined from the equation above, the experimental difficulties in determining the values of accurate neutron flux, cross section and the absolute disintegration rate are so great that an easier method usually known as "comparative method" is usually in practice. More accuracy can be accomplished by this method.

B) The "comparative method" is the simultaneous irradiation of samples with standards containing a known proportion of an element being determined. Then the amount of an element in the unknown samples is to be obtained as follows.

(Mass of an element in unknown sample)

$$= \frac{(\text{Mass of the element in standard sample}) \times (\text{Total activity in unknown sample})}{(\text{Total activity in standard sample})}$$

Corrections, of course, have to be made for weight and radioactive decay in each sample.

Nuclear Data for Arsenic

Natural arsenic has only one stable isotope $^{75}_{33}\text{As}$, which upon irradiation with thermal neutrons gives $^{76}_{33}\text{As}$ which has a half-life of 26.4 hours and emits β -particles of maximum energy 2.97 (50%), 2.41 (31%), 1.76 (15%) and 0.36 Mev (3%), together with gamma rays of 0.560, 1.20, 0.64 Mev and others [9]. The activation cross section of ^{75}As (n, γ) ^{76}As reaction is 5.4 ± 1.0 barns and this figure appears considerably high [10].

Experiments

1. Samples.

As shown in Table 1, extracted human teeth for which time was known after the arsenic pulp-devitalization were used as samples. Caries-free teeth were used as normal controls. Arsenous oxide (As_2O_3), Merck's guaranteed reagent, in which any other

radionuclide was not induced following neutron irradiation in pile prior to the experiment, was employed as standard arsenic sample.

2. Neutron irradiation.

In each bombardment, samples were placed in a polyethylene film and heat-sealed, then packed in a polyethylene capsule together with standard arsenic. Neutron irradiation was performed by the pneumatic tube system of the JRR-1 reactor in operation at Japan Atomic Energy Research Institute, having flux of about 10^{11} thermal neutrons/cm²/sec. Irradiation periods varied from two to fifteen hours.

3. Radiochemical separation of arsenic.

Arsenic was isolated from other elements through distillation as the trichloride from concentrated hydrochloric acid solution. Each irradiated sample was transferred to a distillation flask together with 5 ml of concentrated hydrochloric acid and 1 ml of arsenic "carrier" solution (1 mg As/ml).^{*} The flask was warmed gently until the sample tooth was completely solved with the dropwise addition of 30% hydrogen peroxide solution through the dropping funnel into the flask. Following this, another 5 ml of concentrated hydrochloric acid was added to the sample solution with 5 g of cuprous chloride and the distillation of arsenic trichloride was carried on at a temperature not exceeding 107°C. The resultant distillates were received in a vessel containing 2 ml distilled water which was placed in ice bath. The distillates were then transferred into a polyethylene tube for radioactivity counting.

4. Radioactivity counting.

The counting of radioactivity was performed for gamma counts by employment of the Toshiba's single channel gamma ray pulse height analyser with NaI (TI) well-type crystal $\left(1\frac{3''}{4} \times 2''; \frac{3''}{4} \times 1\frac{1''}{2}\right)$. By analysis of radioactive decay curves of the samples, it was possible to compare the radioactivity of sample arsenic with that of standard control arsenic for the same point of time.

5. Chemical yield of the method.

Subsequent to the radioactivity counting, the whole arsenic contained in the distillate was titrated with 0.1 N potassium bromate solution under the presence of methyl orange as an indicator in an effort to determine the recovery of the "carrier" arsenic [11]. Thus the chemical yield of this separation was obtained and corrections for the initial quantity of arsenic in arsenic-devitalized teeth and control normal teeth were duly made.

Results and Discussion

As can be established from the results given in Table 1, the arsenic contents in the arsenic-devitalized teeth were evidently much greater than those in controls. This result is in keeping with those given by OTANI except for the fact that the arsenic values are somewhat less in the present study. He reported that the arsenic ranged in amount from 1.6 to 19.1 μg in the arsenic-devitalized teeth and from 0.6 to 2.2 μg in the control teeth. However, a precise comparison between the two is rendered difficult

^{*} The carrier is prepared by dissolving 1.32 g of arsenic oxide in a small amount of sodium hydrochloride and making up to 1000 ml with distilled water.

TABLE 1
Arsenic determinations on teeth with neutron activation procedure

Sample		Duration after devitalization	Sample weight (g)	As-amount found (μg)	Chemical yield (%)	Corrected As-amount (μg)/tooth	As-concentration $\mu\text{g/g}$ of tooth
Arsenic devitalized teeth	Upper 2nd molar	3 y	1.4356	9.07	65.7	13.80	9.61
	Stumps	3 y	1.4172	3.59	92.1	3.90	2.75
	Stumps	3 y	1.7419	4.98	83.4	5.97	3.43
	Upper lateral incisor	4 y	0.6302	7.66	88.6	8.65	13.73
	Stumps	6 y	1.2547	1.56	74.8	2.09	1.17
	Lower 1st molar	18 y	1.3284	2.54	80.7	3.14	2.36
Control teeth	Upper lateral incisor		0.8386	0.07	93.4	0.07	0.08
	Upper 2nd molar		2.1469	1.05	77.8	1.35	0.36
	Upper 2nd molar		1.6771	0.62	89.6	0.69	0.41
	Lower 1st molar		2.1948	1.93	76.5	2.52	1.15
	Lower 2nd molar		1.7047	0.14	81.7	0.17	0.10

TABLE 2
Nuclear reactions forming of radioactive arsenic nuclides in the nuclear reactor.^{10,12)}

Nuclear Reactions					Induced nuclide	Half-life ⁹⁾
(n, γ)	(n, α)	(n, p)	(n, 2n)	(γ , p)		
			⁵⁷ As		⁷⁴ As	17.5 d
⁷⁵ As	⁷⁹ Br	⁷⁶ Se		⁷⁷ Se	⁷⁶ As	26.4 h
⁷⁶ Ge					⁷⁷ As	38.7 h
	⁸¹ Br	⁷⁸ Se			⁷⁸ As	91.0 m

because of uncertainty as to the amount and the duration of arsenic applied to teeth under experiment.

It is assumed that a greater part of arsenic which migrated into the dental hard tissues will remain in the crown region of teeth, because even in the samples which have the same period of time after pulp-devitalization lesser amount of arsenic concentration has been found in the stump samples. The result of further experiment substantiates this inference.

These findings above given lend support to the belief that the retention of arsenic in the arsenic-devitalized tooth takes place for a fairly long period of time. In reactor, the ^{75}As (n, γ) ^{76}As reaction takes place predominantly, however, it is possible for ^{76}As to be formed by several other reactions starting with such elements as ^{79}Br , ^{76}Se and ^{77}Se , other than ^{75}As , the fast neutrons and gamma rays as well as thermal neutrons are present.

Table 2 lists the nuclear reactions which may induce radionuclides of arsenic in reactor. Moreover, ^{75}As can be formed by the following series of reactions

These reactions may greatly interfere with the arsenic determination by neutron activation analysis. In the present study, however, these influences have been ignored because it was considered that the contents of bromine, germaniums and selenium in human tooth are by no means great.

Summary

The determination of arsenic which migrated into the dental hard tissues was carried out by means of neutron activation analysis. As a results, it was established that the arsenic concentration is greater in the arsenic-devitalized human tooth than in non-devitalized tooth (cf. Table 1). It also became known that the arsenic which migrates into the dental hard tissues remains in that locality extending for a fairly long period of time, though it gradually decreases in amount.

The amount of arsenic thus retained in the tooth for 18 years after arsenic pulp-devitalization is found to be $3.14 \mu\text{g}$ ($2.36 \mu\text{g/g}$ of dental tissues).

References

- [1] OTANI, K. : Studies on the Absorption of Arsenic and its Distribution in Human Body, (in Jap.) Sapporo Igaku Zasshi, **11**, 285 (1957)
- [2] MEINKE, W. W. : Trace-element Sensitivity; Comparison of Activation Analysis with other Methods, Science, **121** ; 177 (1955)
- [3] SMALES, A. A. and PATE, B. D. : The Determination of Submicrogram Quantities of Arsenic by Radioactivation (Part 111) The Determination of Arsenic in Biological Materials, Analyst, **77**, 196 (1952)
- [4] MICHON, R. : Determination of Arsenic in a Sample of Bone by Radioactivation, Ann. Falsif., **49** ; 284, 1956 ; Anal. Abst., **4**, 610 (1957)
- [5] HOLLAND, R. H., WILSON, R. H., ACEVEDO, A. R., MCCALL, M. S., CLARK, D. A. and LANZ, H. C. : A Study of Arsenic in Regular-sized Unfiltered and Filtered Cigarettes, Cancer, **11** : 1115 (1958)

- [6] SMITH, H. : Estimation of Arsenic in Biological Tissue by Activation Analysis, *Anal. Chem.*, **31** ; 1362 (1959)
 - [7] GÖTTE, H. und HATTEMER, J. A. : Radioaktivierungs-analytischer Nachweis von Arsen in Zähnen, *Zeitsch. für Naturforsch.*, **106** : 343 (1955)
 - [8] SAIRENJI, E., YANAGISAWA, S., YAMANO, H., SASAKI, E. and SUZUKI, T. : Tracer Studies of Dental Pulp-devitalizing Agent using Radioactive Arsenic (^{76}As), (in Jap.), *Radioisotopes*, **7** ; 290 (1958)
 - [9] STROMINGER, D., HOLLANDER, J. M. and SEABORG, G. T. : Table of Isotopes, *Rev. Mod. Phys.*, **30**; No. 2 Part II (1958)
 - [10] HUGHES, D. J. and SCHWARTZ, R. B. : Neutron Cross Sections (2nd Edition), U. S. Atomic Energy Commission, BNL-325 (1958)
 - [11] TREADWELL, F. P. and HALL, W. T. : Analytical Chemistry, Vol. II (9th Edition), p. 628 (1951)
 - [12] SMALES, A. A. : "Neutron-Activation Analysis" in Tracer Analysis edited by Yoe, J. H. and Koch, H. J. Jr., John Wiley & Sons, Inc., New York (1957)
-