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THE QUANTITATIVE ANALYSIS OF Sr, Au, Br, Mn AND Na IN NORMAL HUMAN ENAMEL AND DENTINE BY NEUTRON ACTIVATION AND HIGH RESOLUTION GAMMA SPECTROMETRY*

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Introduction

THE concentrations of some of the elements in normal human enamel and dentine that give rise to short-lived radioisotopes, Ca, Na, Al, Mg and Cl, were determined by means of instrumental activation analysis and the results reported in a previous paper (Retief *et al*, 1970). Subsequently the concentrations of some of the elements that give rise to long-lived radioisotopes, Cr, Ba, Sb, Ag, Zn, Co and Fe were determined by the same instrumentation (Retief *et al*, 1970). The purpose of the present study was to attempt to analyse quantitatively further elements in these tissues.

By modifying the irradiation conditions another four elements, Sr, Au, Br and Mn, were so analysed in addition to Na, which previously was determined with other short-lived radioisotopes. Söremark and Samsahl (1961, 1962) investigated the concentrations of these five elements and six others by gamma-ray spectrometry. The gamma activity of the irradiated samples was measured by a NaI(Tl) detector in combination with a 256 channel gamma spectrometer. Because of the poor resolution of this detector they used a chemical separation procedure by means of a series of ion exchange columns to determine these elements quantitatively.

As it has been shown that instrumental activation analysis can be successfully employed for the quantitative analysis of a number of elements in normal human enamel and dentine (Retief *et al*, 1970), this analytical technique was applied in the present investigation.

Experimental Methods

(a) *Preparation of the enamel and dentine samples.*

Freshly extracted, sound human teeth were used. Debris and tartar were removed and the teeth thoroughly washed in deionised water for a few minutes. They were dried in an oven at 105°C and the enamel was mechanically separated from the dentine by chipping. The dentine was obtained from the root portion and no attempt was made to separate the cementum. The enamel and dentine were ground to a fine powder in an agate mortar and dried to constant weight at 105°C.

(b) *Procedure.*

The enamel and dentine samples were accurately weighed in separate quartz ampoules which were then sealed. 100 mgs of each sample were taken for the analysis of Sr and 200 mgs for the analysis of Au, Br, Mn and Na. Standard samples were prepared by weighing a known volume of a mixed solution into quartz ampoules. This solution contained known amounts of Sr, Au, Br, Mn and Na, and salts of eight other elements present in enamel and dentine. The standard samples contained approximately the same amounts of these elements as are present in 100 mgs and 200 mgs enamel and dentine respectively. Analytical grade reagents were used in the preparation of all the standards. The

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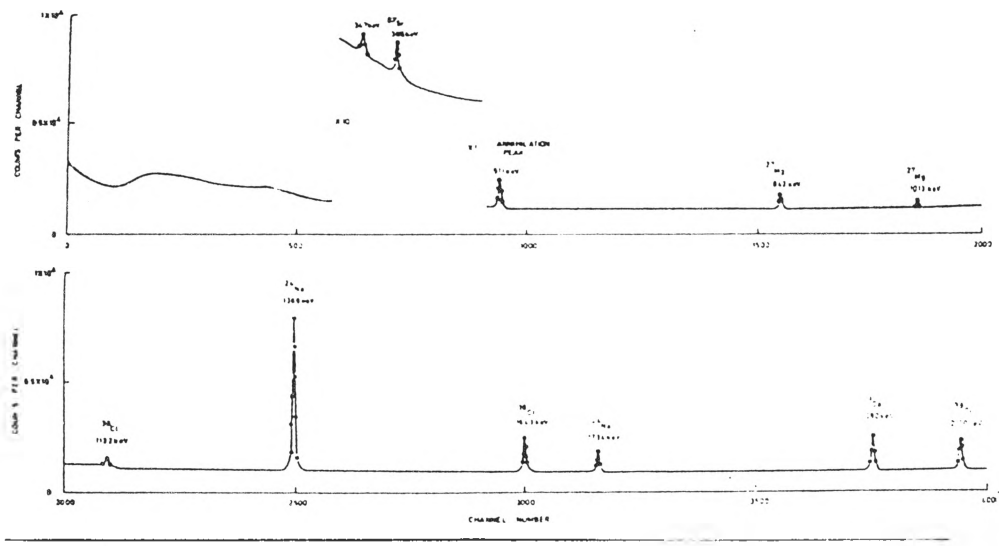

FIG. 1. Gamma spectrum of enamel sample irradiated for 15 minutes.

standard liquid mixtures were then carefully evaporated to dryness, after which the quartz ampoules were sealed.

Enamel and dentine samples were irradiated with standard samples. For the determination of Sr, the three quartz ampoules were sealed in a polyethylene rabbit and irradiated in the pneumatic facility of the reactor for 15 minutes in a thermal neutron flux of 1.2 x 10^{12}n. cm^{-2} $sec.^{-1}$. The reactor, SAFARI-1, is an ORR type reactor of the South African Atomic Energy Board at Pelindaba. For the analysis of Au, Br, Mn and Na the three samples were sealed in an aluminium can completely lined with cadmium. They were irradiated for 12 hours in the poolside facility of the reactor in a thermal neutron flux of approximately 2 x 10^{13}n.cm^{-2} sec^{-1}. The measurement of their gamma activity was commenced 15 minutes after irradiation for the analysis of Sr, and 15 hours after irradiation for the analysis of Au, Br, Mn and Na. The irradiated samples were placed at 20 cm distance from the Ge(Li) detector —a 50 cm^3 coaxial Ge(Li) diode (Princeton Gamma Tech.) connected to an uncooled TC 135M Tennelec preamplifier. The output pulses were amplified by a TC 200 Tennelec amplifier and analysed by an Intertechnique 4000 channel analyser (model SA 44). Data for peak analysis were obtained on punched tapes by a Tally P-120. Yule's (1968) smoothed first derivative method was applied to obtain the peak counts under the photopeaks of interest.

TABLE I: Nuclear data of Sr, Au, Br, Mn and Na

Stable Isotope	*Abundance*	*Activation cross section (Barns)*	*Daughter radio-nuclide*	*Half-life radio nuclide*	*γ-ray photopeak measured keV*
^{86}Sr	9.86	0.8	^{87}Sr	2.8 h	388
^{197}Au	100	98.8	^{198}Au	64.8 h	411
^{81}Br	49.46	0.26	^{82}Br	35.3 h	776
^{55}Mn	100	13.3	^{56}Mn	2.57 h	847
^{23}Na	100	0.13	^{24}Na	15.05	1368

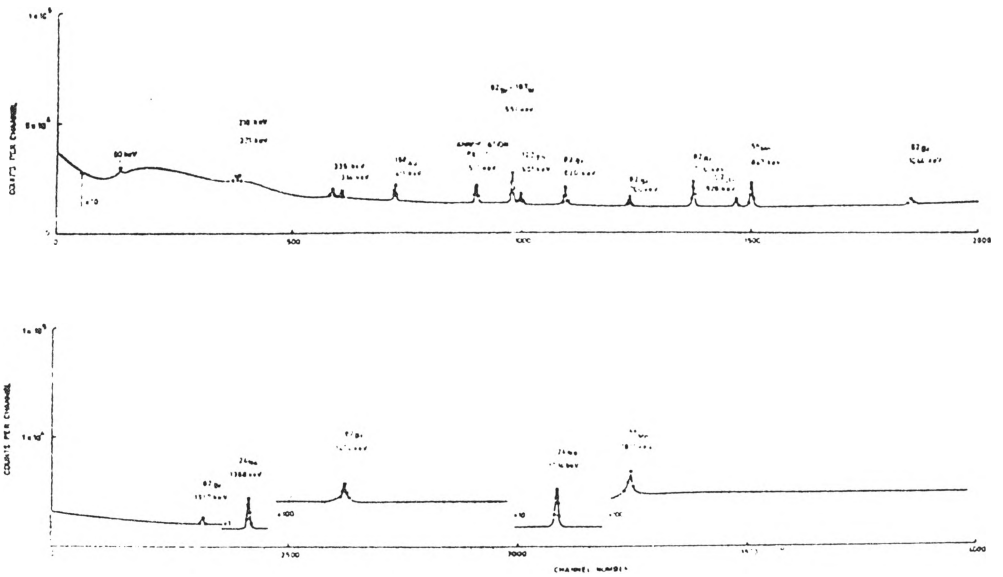

FIG. 2. Gamma spectrum of dentine sample irradiated in a cadmium shield for 12 hours.

(c) *Nuclear data.*

The radionuclides of Sr, Au, Br, Mn and Na produced by thermal neutron activation and the relevant nuclear data are given in Table I.

RESULTS

A typical γ-spectrum from an enamel sample irradiated for 15 minutes is shown in Fig. 1. The ^{87}Sr photopeak at 388 keV is well separated from other photopeaks. The γ-spectrum obtained from a dentine sample after irradiation in a cadmium shield for 12 hours is indicated in Fig. 2. It is clear that the 411 keV, 776 keV, 847 keV and 1368 keV photopeaks of ^{198}Au, ^{82}Br, ^{56}Mn and ^{24}Na respectively are well separated from the other peaks in this spectrum. These photopeaks can therefore be used as a measure of the strontium, gold, bromine, manganese and sodium concentrations in normal enamel and dentine. The concentrations of these elements in enamel are shown in Table

TABLE II: The concentration of Sr, Au, Br, Mn and Na in normal human enamel.

Element	*Number of samples analysed*	*Mean conc. ppm*	*Standard error of mean*	*Standard deviation*	*95% confidence interval for the true mean*
Sr	7	111.19	3.71	9.86	102.83 - 119.55
Au	7	0.11	0.03	0.07	0.05 - 0.17
Br	8	33.79	2.02	5.71	29.23 - 38.35
Mn	4	0.59	0.02	0.04	0.55 - 0.63
Na	9	0.70%	0.02	0.05	0.66 - 0.74

TABLE III: The concentration of Sr, Au, Br, Mn and Na in normal human dentine.

Element	*Number of samples analysed*	*Mean conc. ppm*	*Standard error of mean*	*Standard deviation*	*95% confidence interval for the true mean*
Sr	6	94.33	4.72	11.47	83.66 - 105.00
Au	8	0.07	0.01	0.04	0.04 - 0.10
Br	6	114.37	1.15	2.80	111.77 - 116.97
Mn	5	0.63	0.02	0.05	0.58 - 0.68
Na	9	0.64%	0.01	0.04	0.60 - 0.68

TABLE V. Dentine: Comparison of results of other investigations with present study.

	Elements					
Author	*Sr ppm*	*Au ppm*	*Br ppm*	*Mn ppm*	*Na %*	*Method*
Drea [1936]	+			+		Direct current spectrum excitation.
Lowater, [1937] Murray	Present			Weak	Present	Spectrographic analysis.
Soremark, [1965] Samsahl	69.8	0.03	4.0	0.19	0.75	Neutron activation. Chemical separation. NaI (Tl) detector.
Calonius, [1965] Visapää	10 - 1000	—	>10,000	—		X-ray emission spectrography.
Lundberg, [1965] Söremark, Thilander	64	$<10^{-4}$		0.56	0.85	Neutron activation. Chemical separation. NaI (Tl) detector. Unerupted teeth.
Hardwick, [1967] Martin	100 - 1000	<1	10 - 100	10 - 100		Mass spectrometry. Approximate estimation.
Battistone, [1967] Feldman, Reba				0.25		Neutron activation. Chemical separation. NaI (Tl) detector.
Present study	94	0.07	114	0.63	0.64	Instrumental activation analysis.

TABLE IV. Enamel: Comparison of results of other investigations with present study.

	Elements					
Author	*Sr ppm*	*Au ppm*	*Br ppm*	*Mn ppm*	*Na %*	*Method*
Drea [1936]	+			+		Direct current spectrum excitation
Lowater, [1937] Murray	Present			Weak	Present	Spectrographic analysis.
Steadman, [1958] Brudevold, Smith	100 - 125					Spectrographic analysis.
Söremark, [1961] Samsahl	93.5	0.02	4.6	0.54	1.16	Neutron activation. Chemical separation. NaI (Tl) detector.
Calonius, [1965] Visapää	10 - 1000	—	100— 10.000	—		X-ray emission spectrography.
Lundberg, [1965] Söremark, Thilander	83	$<10^{-4}$		1.12	0.97	Neutron activation. Chemical separation. NaI (Tl) detector. Unerupted teeth.
Nixon, [1966] Livingston, Smith				0.30— 2.01		Neutron activation. Chemical separation. NaI (Tl) detector.
Little, [1966] Steadman	60 - 100			4		Spectrographic analysis.
Hardwick, [1967] Martin	100 - 1000	<1	100— 1000	10— 100		Mass spectrometry. Approximate estimation.
Battistone, [1967] Feldman, Reba				0.60		Neutron activation. Chemical separation. NaI (Tl) detector.
Present study	111	0.11	34	0.59	0.70	Instrumental activation analysis.

II and in dentine in Table III. The results are based on the dry weight of the enamel and dentine heated to constant weight at 105°C.

DISCUSSION

The enamel samples were obtained by chipping. Its separation from dentine by this method is a slow process and does not lead to its complete recovery. In addition, its contamination by dentine is unavoidable especially if large amounts are collected. Its removal by grinding with a carborundum separating disc was considered, but the idea was abandoned because neutron activation analysis showed it to contain Mn, Cu and Al. Battistone *et al* (1967) determined the effect of tissue separation procedures on the Mn concentration in human enamel and dentine, which they separated for analysis by two methods: chipping with polyethylene-protected instruments, and grinding with tungsten carbide burs or small tapered diamond cutting stones. They reported that the Mn values in enamel were always higher when grinding procedures were used. Tungsten carbide burs gave an increase of up to 150 per cent and diamond stones up to 50 per cent compared with the results obtained by chipping.

Manley and Hodge (1939) developed a method designed to apply a centrifugal technique to the usual flotation procedure for the separation of the two tissues. It enabled them to prepare 99.4 per cent pure enamel and 99.7 per cent pure dentine with approximately 10 per cent loss of material. Calonius and Visapää (1965) did a semi-quantitative analysis by x-ray emission spectrography. Bromine concentrations of up to 10,000 ppm were recorded. They adopted the technique of Manley and Hodge to separate the enamel from the dentine. This technique entails the use of acetone-broform mixtures, which explains the very high values obtained; and apart from the obvious contamination with bromine, no such mixture is sufficiently pure to prevent contamination of the enamel and dentine with other elements prior to irradiation. This method of separation must be excluded when employing activation analysis.

The concentrations of Na, Sr and Mn have been extensively investigated. The results obtained in this investigation for these three elements are similar to those described by other workers (Tables IV and V). The mean concentration of sodium was 0.70 per cent in enamel and 0.64 per cent in dentine. These figures are slightly higher than those previously reported (Retief *et al*, 1970). Under the present irradiation condition the ^{27}Al (n,α) ^{24}Na and ^{24}Mg (n,p) ^{24}Na reactions cannot be ignored as they are responsible for the higher sodium concentrations.

There is little in the literature regarding the concentrations of Au and Br. The present authors found slightly higher values for the Au concentration than did Söremark and Samsahl (1961, 1962). Thilander *et al* (1965), who investigated its concentration in unerupted teeth, detected it in only minute quantities—less than 10^{-1} ppm. They suggested the high concentration in erupted teeth to be due to contamination by gold restorations in neighbouring teeth. It is extremely difficult to obtain homogenous mixes of gold by grinding in a mortar, which could explain the standard deviation of approximately 70 per cent. In this study the bromine concentration was much higher than that obtained by Söremark and Samsahl. Its concentration in dentine is approximately three times that in enamel.

The cadmium shield was used in part of the investigation because this element absorbs most of the thermal neutrons to which samples are exposed during irradiation. As a result elements which possess activation cross-sections for thermal neutrons only, will be slightly activated. Consequently the interference from these elements, for instance Ca, P, Na, Mg and Cl, will be markedly reduced. On the other hand, those which have high resonance integrals such as Au, Br and Mn will be activated to a greater extent. These elements are present in teeth in low concentrations and this technique renders their quantitative analysis possible.

SUMMARY

The concentrations of Sr, Au, Br, Mn and Na in normal human enamel and

dentine were determined employing instrumental neutron activation analysis. Their mean concentrations in enamel were 111, 0.11, 34, 0.59 ppm and 0.70 per cent, and in dentine 94, 0.07, 114, 0.63 ppm and 0.64 per cent respectively.

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