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ANALYSIS OF FLUORINE BY NUCLEAR REACTIONS AND APPLICATION TO HUMAN DENTAL ENAMEL.

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Abstract :

Nuclear reactions induced on Fluorine by low energy protons are investigated, thick target excitation yield curves and tables for $^{19}F(p,p'\gamma)^{19}F$ and $^{19}F(p,\alpha\gamma)^{16}O$ reactions are given between 0.3 and 2.5 MeV. Interferences from other nuclear reactions, detection limits and sensitivity for Fluorine detection are investigated.

After a wide investigation of the repartition of Fluorine in tooth enamel it is concluded that there is an equilibrum of the concentrations between tooth and saliva which is rapidly restored after the perturbation introduced by the external treatments.

I. PROMPT GAMMA-RAYS FROM PROTON BOMBARDMENT OF FLUORIDE SAMPLES.

The technique of Fluorine analysis by low energy nuclear reaction has often been described [1] [2] [3] and the application to Fluorine concentration determination is now routinely used in different laboratories. An intense gamma-ray emission is observed when Fluorine is bombarded with low energy protons :

a) low energy gamma-rays from inelastic scattering ($E\gamma$ = 110 and 197 keV),

b) high energy gamma-rays from $(p,\alpha\gamma)$ reactions ($E\gamma$ = 6.13, 6.72 and 7.12 MeV).

At low energy isolated resonances in the cross-section curves can be used for depth profile analysis, at higher energy the resonances overlap and cross sections are monotonic function of the proton energy.

The γ-ray yield from a thick sample of CaF_2 was detected at different proton energy, the data were corrected for stopping power and concentrations, in order to correspond to a sample of pure Fluorine. The number of gamma-rays emitted by an homogeneous thick sample bombarded with protons of energy E_o is then given by [4]

$$N_s = N_\gamma \, C_S \, \frac{S(\bar{E})}{S_s(\bar{E})} \, (\mu C \times \text{Sterad.})^{-1} \qquad (1)$$

where N is the number of gamma-rays detected at energy E_o.

N_γ is the number given in the table.

C is the concentration of Fluorine in the sample.

$S(\bar{E})$ and $S_s(\bar{E})$ are the stopping power parameter of Fluorine of the sample (in MeV/g cm^2) and of the standard, respectively.

$\bar{E}$ is the proton energy for which the yield has half the value it has at energy E_o.

For bulk analysis the sample is bombarded with 2.5 MeV protons, γ-rays are detected in a Ge-Li detector for low energy γ-rays, in a large NaI scintillator for high energy gamma-rays. The concentration is obtained by comparison with a standard by application of the following formula [4].

$$C_s = C_{st} \frac{N}{N_{st}} \frac{S_s(\bar{E})}{S_{st}(\bar{E})} \qquad (2)$$

The accuracy of the determination was tested by making calibration curves with standard samples and also by comparing the results obtained by this technique with chemical determinations on sample of unknown composition. The absolute accuracy is better than 1% for concentration larger than 0,001, the sensitivity limit for quantitative determination is about 1 p.p.m.

1) $^{19}F(p,p'\gamma)^{19}F$ reaction.

Two gamma-ray lines are observed in spectra from the $^{19}F(p,p'\gamma)^{19}F$ reaction, they correspond to $E\gamma = 110$ keV and $E\gamma = 197$ keV, the thick sample yield is the same for both radiations for 2 MeV protons, above this energy the 197 keV gamma-ray emission is more intense. A complete tabulation of the thick target excitation yield is given in Table I and the corresponding excitation curves are represented on fig.1-2. From these data, the number of gamma-rays from bombardment of a given sample can be predicted by using formula (1). A narrow resonance is present at $E_R = 938$ keV ($\Gamma_R = 4.5$keV) The corresponding plateau is clearly visible in the excitation curve, below this energy the reaction is not very intense, above this energy the excitation yield curve reveals the presence of many resonances superposed to a continuous amplitude.

A serious handicap in the utilization of these gamma-rays for quantitative analysis is the presence of an important continuous spectrum from higher energy gamma-rays(Compton effect), this effect can be reduced by using a high resolution Ge-Li detector (1 keV) of small thickness. The estimated sensitivity limit is then 10 p.p.m.

A possible first order interference is the $^{18}O(p,\gamma)^{19}F$ reaction with the emission of 197 keV gamma-rays, the intensity is very small and does not affect seriously the determinations even in presence of large concentrations of oxygen. The emission of 110keV gamma-ray was not observed in the bombardment of oxygen with [illegible] MeV protons. This interference can be resolved in two ways :

a) by measuring the ratio Nγ(110 keV)/Nγ(197 keV) which must be identical for a Fluorine standard and for the sample, this ratio is also obtained from Table I.

b) by measuring the intensity of the 495 keV gamma-ray yield from the $^{16}O(p,\gamma)^{17}F$ reaction for 2.2 MeV protons. The number of 197 keV gamma-rays from the interfering reaction is then given by Nγ(197keV 0.5 Nγ(495 keV).

2) $^{19}F(p,\alpha\gamma)^{16}O$ reaction.

Several lines are seen in the spectra from the $^{19}F(p,\alpha\gamma)^{16}O$ reaction detected with a large volume (30c.c.) Ge-Li detector (fig.4), they correspond to full energy, one-escape and two-escape peaks of the 6.131, 6.916 and 7.115 MeV gamma-rays. The more intense is the 6.131 MeV group γ_3, the two other groups γ_1 and γ_2 have comparable intensity and are strongly affected by Doppler effects, the life-time of the corresponding levels in ^{16}O being short enough for disintegration to take place before slowing down in the sample. A complete tabulation of the thick target yield is available while the corresponding excitation curves are represented on fig.3. Many resonances are presen and can be used for depth profile analysis, the step height I_R of the corresponding plateau in the excitation curve is proportional to the product $\sigma\Gamma$ of the cross-section at resonance by the FWHM Γ. The following narrow resonances are currently used for depth profile analysis.

E_p (keV)	6-7 MeV	E_o (keV)	110 keV	197 keV	6-7 MeV	E_p (keV)	110 keV	197 keV	6-7 MeV
330	1.0	920	85	-	185	1640	2761	736	1048
340	5.5	935	317	156	→ 234	1700	3016	944	1220
350	5.7	950	370	170	259	1730	3093	1068	1350
375	5.9	980	414	171	265	1750	3149	1152	1389
400	6.1	1030	443	171	279	1815	3253	1509	1508
450	6.5	1080	463	172	286	1880	3546	2311	1872
475	6.8	1090	488	230	289	1915	3892	3153	2153
485	8.3	1105	491	230	300	1930	4270	3559	2274
495	8.3	1130	496	259	312	1950	5181	4508	2367
520	9.0	1156	502	274	322	1980	6128	6214	2937
570	10.2	1210	580	289	376	2030	6837	8795	3651
595	13.7	1250	614	303	399	2080	7377	11782	4541
620	16.1	1263	717	304	407	2160	7823	12798	5500
645	18.2	1280	778	307	425	2210	7976	13817	-
660	20.7	1290	779	309	437	2317	11420	18088	-
670	28.5	1315	1015	319	458	2370	16106	23615	-
680	28.5	1325	1015	329	460				
690	30.5	1335	1015	339	463				
740	31.7	1345	1016	349	480				
780	32.0	1350	1032	368	509				
790	32.4	1365	1080	427	554				
820	35.4	1375	1111	466	661				
830	37.2	1400	1227	584	765				
835	38.5	1420	1850	592	798				
845	40.4	1430	1924	596	816				
870 →	120.4	1475	2384	621	868				
890	166.1	1550	2715	675	930				
900	175.7	1600	2759	705	1002				
910	179.	1610	2760	706	1047				

TABLE I. Thick target excitation yield for the (p,p'γ) and (p,αγ) reaction on ^{19}F. The yield is given in $(\mu C.ster)^{-1}$ for a pure Fluorine sample.

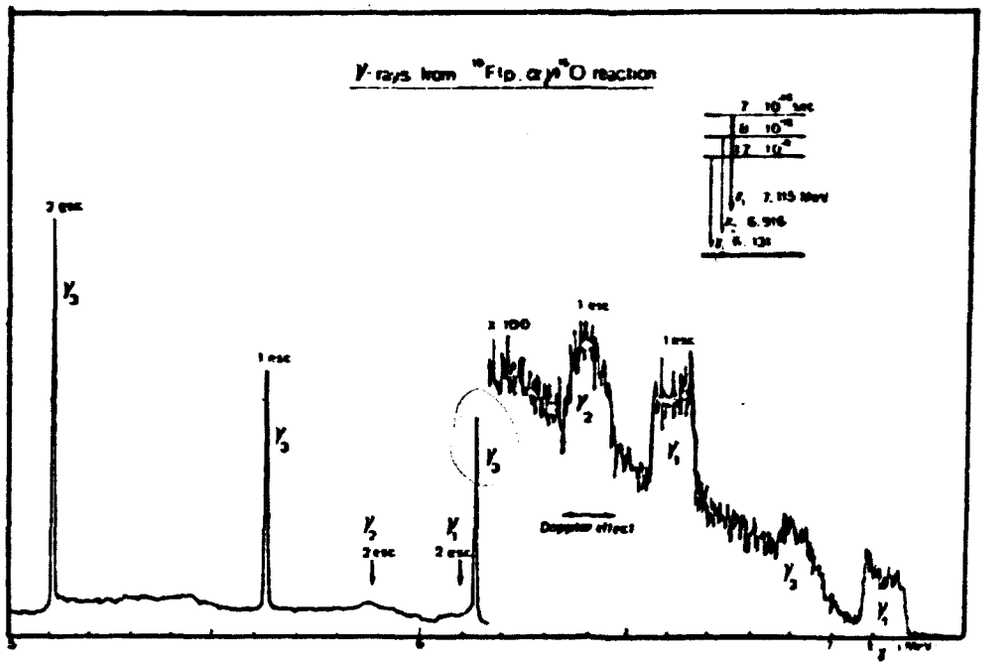

FIG. 4

E_R = 340 keV Γ_R = 2.4 keV I_R = 6.000
E_R = 872 keV Γ_R = 4.5 keV I_R = 126.000
E_R = 935 keV Γ_R = 8.6 keV I_R = 70.000

None of these resonances has a pure B-W shape, a continuous background being superposed to the resonant amplitude.

The gamma-ray intensity from the competiting $^{15}N(p,\gamma)^{16}O$ reactions is very small, for 2 MeV proton the ratio $N\gamma(^{15}N)/N\gamma(^{19}F)$ is lower than $5\ 10^{-5}$. Another interference from Nitrogen is possible when low resolution detectors are used, it originates from the $^{14}N(p,\gamma)^{15}O$ reaction giving a gamma-ray peaks emission of 6,79 MeV without appreciable Doppler broadening. The presence of Nitrogen can be detected by the observation of 4.43 MeV gamma-rays from the $^{15}N(p,\alpha\gamma)^{12}C$ reaction, the intensity being 100 times higher than for the 6,79 MeV radiation above 2.5 MeV.

3) Depth profile analysis.

The energy spread in the proton beam, the resonance width and the energy straggling in the sample determine the depth resolution in profile analysis. The depth resolution at the surface of the sample (small energy loss) must be calculated using Vavilov distributions[5], in Fluorine analysis the resonances have large width and the distributions are strongly modified by convolution with the resonance curve, for large depth ($x > 10^{-4}$ g cm^{-2}) the resulting distribution can be considered as gaussian-like, the FWHM is given for normal incidence by :

$$\Gamma = \sqrt{\gamma_0^2 + \Gamma_R^2 + \Gamma_s^2}$$

where : γ_0 is the FWHM of the beam energy distribution,
Γ_R is the natural width,
Γ_s is the straggling width given by :

$$\Gamma_s = 0{,}93\ z \sqrt{x\ \tilde{Z}/\tilde{A}}$$

The maximum depth and thickness that can be analysed depends on the energy of neighbouring resonances. The lower energy neighbouring resonance position determines the maximum sample thickness s_{max} which can be analysed while the high energy neighbour determines the maximum depth x_{max} which can be analysed. The following resonances can be used for depth profile analysis, the given parameters correspond to tooth enamel which is equivalent to a pure Silicon matrix.

E_R(keV)	Γ'_R(keV)	$S_{Si}(E_R)$	x_{max}	S_{max}	Resolution ($x=x_{max}$)
340	2.4	375	($3.2\ 10^{-4}$)	$3.2\ 10^{-4}$	$3.4\ 10^{-5}$
872	4.7	189	$3.3\ 10^{-4}$	$3.3\ 10^{-4}$	$6.8\ 10^{-5}$
935	8.1	183	($3.3\ 10^{-4}$)	$3.3\ 10^{-4}$	$8.4\ 10^{-5}$
1373	12.4	145	($1.8\ 10^{-4}$)	$1.8\ 10^{-4}$	$1.0\ 10^{-4}$

All these data are given in g cm^{-2}, the resonance energy and width are given in the laboratory system. From fig.3 it is concluded that the 872 keV resonance is the more intense, the maximum depth can be analysed without interfering with the 935 keV resonance is $6.8\ 10^{-5}$ g cm^{-2} or about 1.3µm in tooth enamel.

II. TOOTH ENAMEL ANALYSIS.

1) The sample structure.

The important problem of dental caries following the dissolution of the enamel structure under the action of acid substances was studied for many years by means of different techniques, the Fluorine ion being supposedly playing an important action in the inhibition of enamel dental caries. The dental enamel is at 95% a layer of apatite, 500µm thick, in which the OH radical is partly substitued by Fluorine ions giving a concentration of 1 to 5‰ of Fluorine.

Nuclear resonance is an unvaluable probe in dental enamel analysis since X-ray techniques (electron microprobe) are subject to errors from strong absorption of the soft X-ray radiation another advantage is the possibility of non destructive depth profile analysis with very small diameter beams.

NMR studies indicate that the Fluorine ion would migrate along the C axis of the hydroxyapatite crystal, preventing further migration of OH ions.

However the enamel structure is very different from the single crystal model, X-ray diffraction spectra show a widening of X-ray lines which indicates that the sample is a superposition of cristallites the size of which ranges between 300 and 400 Å. The intervals between these cristallites is filled by an organic network

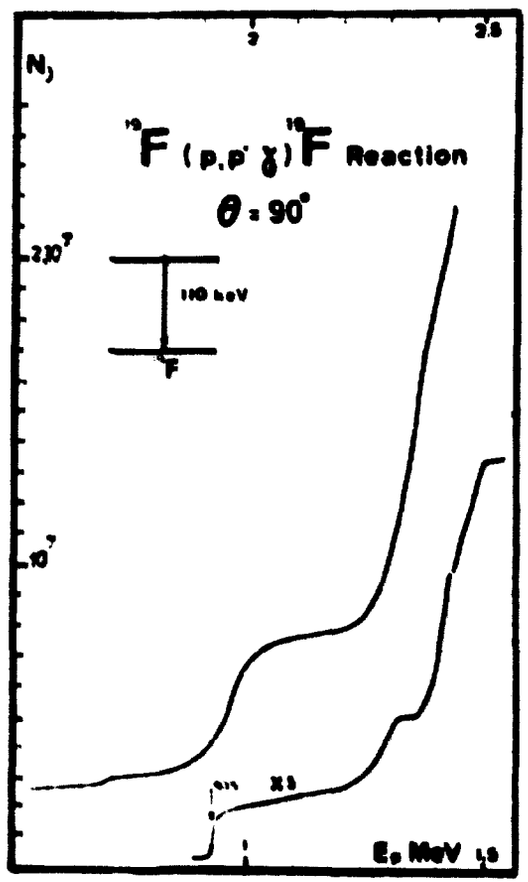

FIG.1

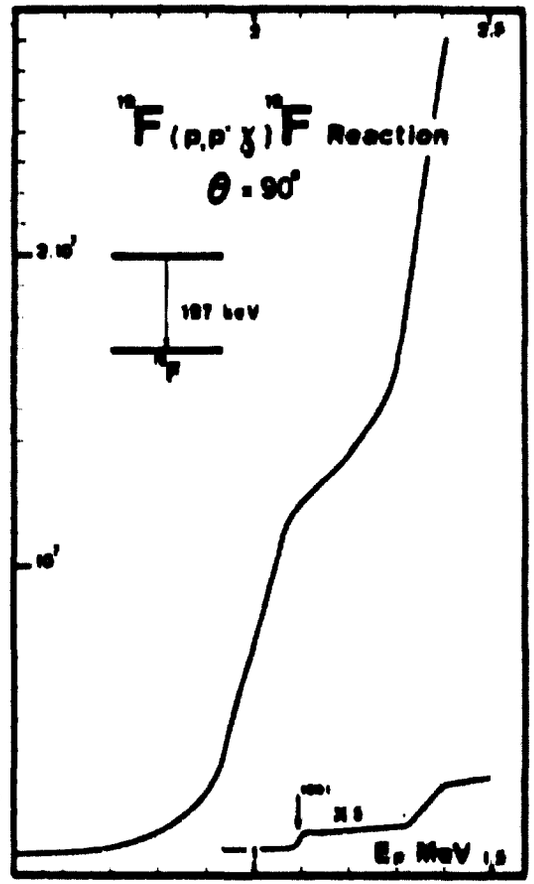

FIG.2

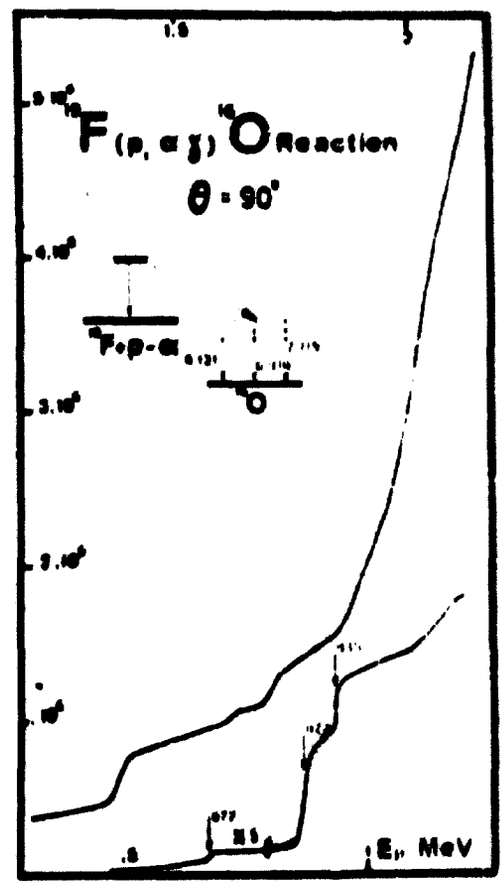

FIG.3

in which the ^{-}F ion can migrate. For these reasons the measurements have to be done on tooth enamel rather than on apatite crystals and they should reproduce as close as possible the conditions of real life.

2) Experimental method.

Teeth are bombarded with the proton beam from the 3 MeV L.A.R.N. Van de Graaff accelerator, very small beam currents are used in order to reduce radiation damage effects. The sample is sealed on an Aluminium frame, the tooth enamel being an excellent insolator, the distance between the beam spot and the Aluminium was kept as small as possible, even so, important charge effects are observed. In an excitation curve taken on the 872 keV resonance, the step corresponding to the resonance is shifted toward higher proton energies, shifts as high as 15 keV are observed. This effect is due to the accumulation of electric charges in surface increasing the local potential on the target, the protons are then slowed down before reacting the surface. This effect is impossible to eliminate completely, fortunately, the shift is constant when the samples are bombarded in same experimental conditions, a permanent shift of 10 keV being present in all the measurements (fig.5).

The 872 keV resonance in the $^{19}F(p,\alpha\gamma)^{16}O$ reaction was choosen because of the high intensity of this reaction, it is not the best resonance for deep analysis but in the case of tooth the Fluorine concentration gradient is large at the surface and the influence of the lower energy resonance is small, on the other hand the observed diffusion region in enamel does not exceed 1µm in thickness.

Excitation curves are measured on each sample in order to obtain the Fluorine concentration after various treatments. The surface of each tooth is divided into three regions the first is left rough, the second is polished with pumice paste ir order to remove a surface layer of about 100µm(P), the third region is polished and then treated with different fluoridated products (P+F), all these treatments are done in vivo. The tooth is left in mouth for a given

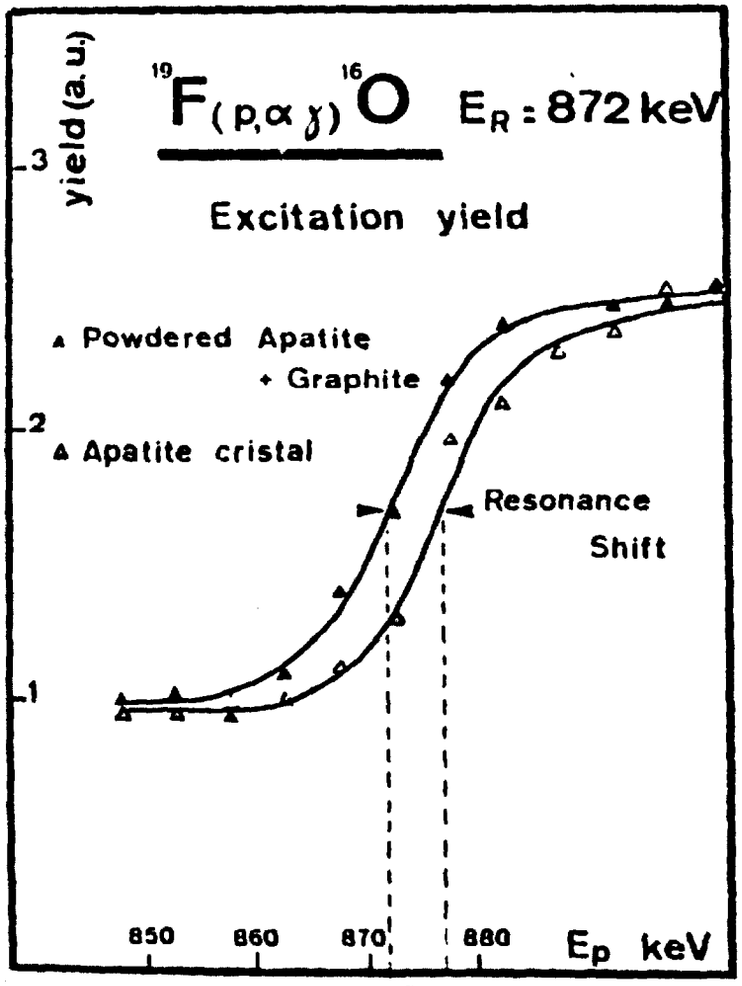
yield (a.u.)
$^{19}F_{(p,\alpha\gamma)}{}^{16}O$ E_R : 872 keV
Excitation yield
▲ Powdered Apatite
+ Graphite
▲ Apatite cristal
Resonance
Shift
3
2
1
850
860
870
880
Ep keV

FIG. 5

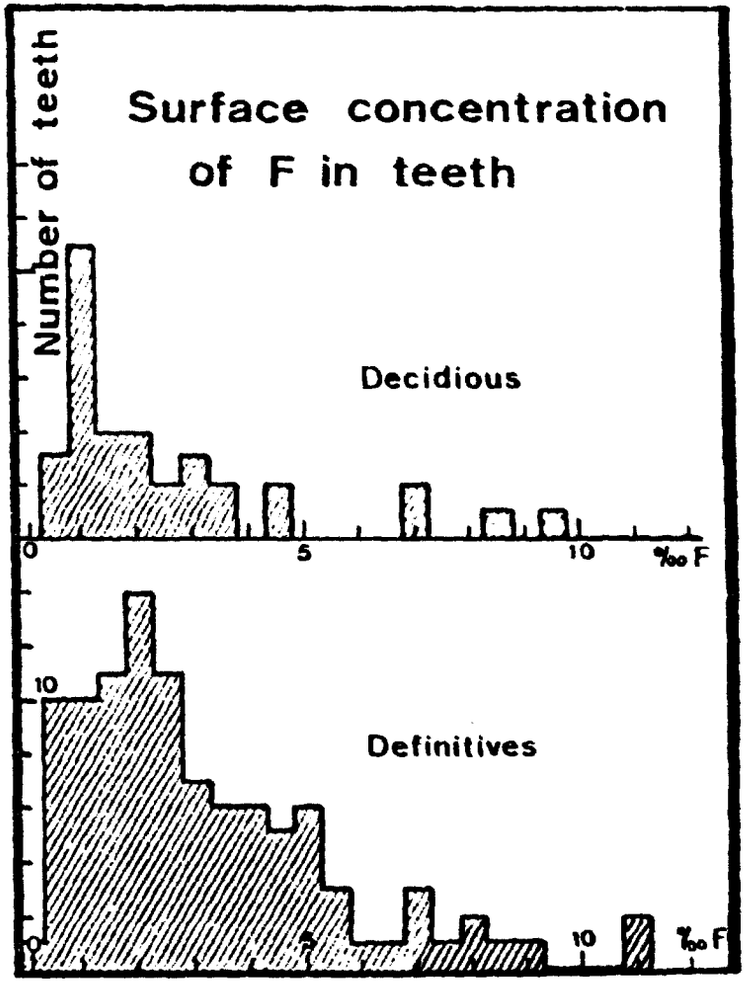
Number of teeth
Surface concentration
of F in teeth
Decidious
0
5
10
‰ F
Definitives
10
0
5
10
‰ F

FIG. 6

time and then extracted before analysis. Each region is analysed for Fluorine concentration and the results are compared.

The Fluorine concentration is extremely variable from tooth to tooth and only average results may have a signification. For this reason a great number of data must be obtained before drawing conclusions.

3) Measurements.

A number of teeth was first explored in order to detect systematic effects in Fluorine distributions. A beam spot of 100µm was used and a scanning was made across the different surface regions, strong concentration variations are observed which are found to be purely random so that only average values are meaningfull. Average values are obtained by using a 500µm diameter beam spot, and by moving the sample back and forth during the measurement. A systematic study of concentration in more than 150 untreated teeth of different origins has revealed that the Fluorine concentration distribution is skew with an average value of 0,25% for normal teeth and 0,15% for decidious teeth (milk-teeth). (fig.6).

For depth profile analysis the 872 keV resonance was used with detection of the high energy gamma-rays in a 4"x3" NaI scintillator. In order to evaluate straggling effects the distributions obtained by making the convolution product of the Vavilov distributions with the Breit Wigner distribution of 4.8 keV FWHM was calculated for different energy losses. The results of this calculation are presented in fig.7, they are used for unfolding of the excitation yield curves. The Fluorine distribution is obtained by using trial profile concentrations and taking the "convolution" product with the distributions of fig.7. The results are given in fig.8-9 where the profile curves corresponding to an average determination on 17 teeth are given. In a first run (fig.8) teeth are treated and extracted after what they are analysed by taking excitation curves at resonance on a 50 keV energy range on the two regions. No appreciable concentration modifications are observed when extracted teeth are kept in

a dry atmosphere for a long time. The curves in fig.8 show that in the treated region a large enrichment in Fluorine is detected on a depth of 0.1 to 0.3µm. (the first 0.1µm being uncertain, the concentration is represented by a dashed line). In a second run of measurements, teeth are left in mouth during 10 days before extraction, no appreciable difference is detected between polished and fluoridated regions (fig.9). A similar phenomenon was observed when teeth are kept in distilled water.

4) Conclusion.

Fluorine migration in teeth enamel is observed when the rough surface is eliminated by polishing and treatment with different fluoridated compounds (Fluocaril dental frost). This fluoration does not disappear when the tooth is kept in dry atmosphere. On the contrary the enrichment effect is practically absent after a few days when the tooth is kept in contact with saliva. It is then supposed that the atoms of Fluorine are eliminated by ion exchange phenomena in saliva. The hypothesis of exchange with Chlorine ions was made and the Cl concentration was measured by X-ray fluorescence induced by proton, no appreciable variation was observed. A similar phenomenon being observed when teeth are kept in distilled water, the possibility arises of exchange with OH ions although the migration energy of a F^- ion is only 0.48 eV while it is 2.1 eV for an OH^- ion. Another explanation would be that the fluoride ions introduced by the treatment do not appreciably migrate into the cristallites but would simply be introduced between the cristallites through the organic matrix. A possible test of this hypothesis is to take NMR spectra from enamel powder, unfortunately the concentration is so low that the experiment is beyond the sensitivity limits of this technique.

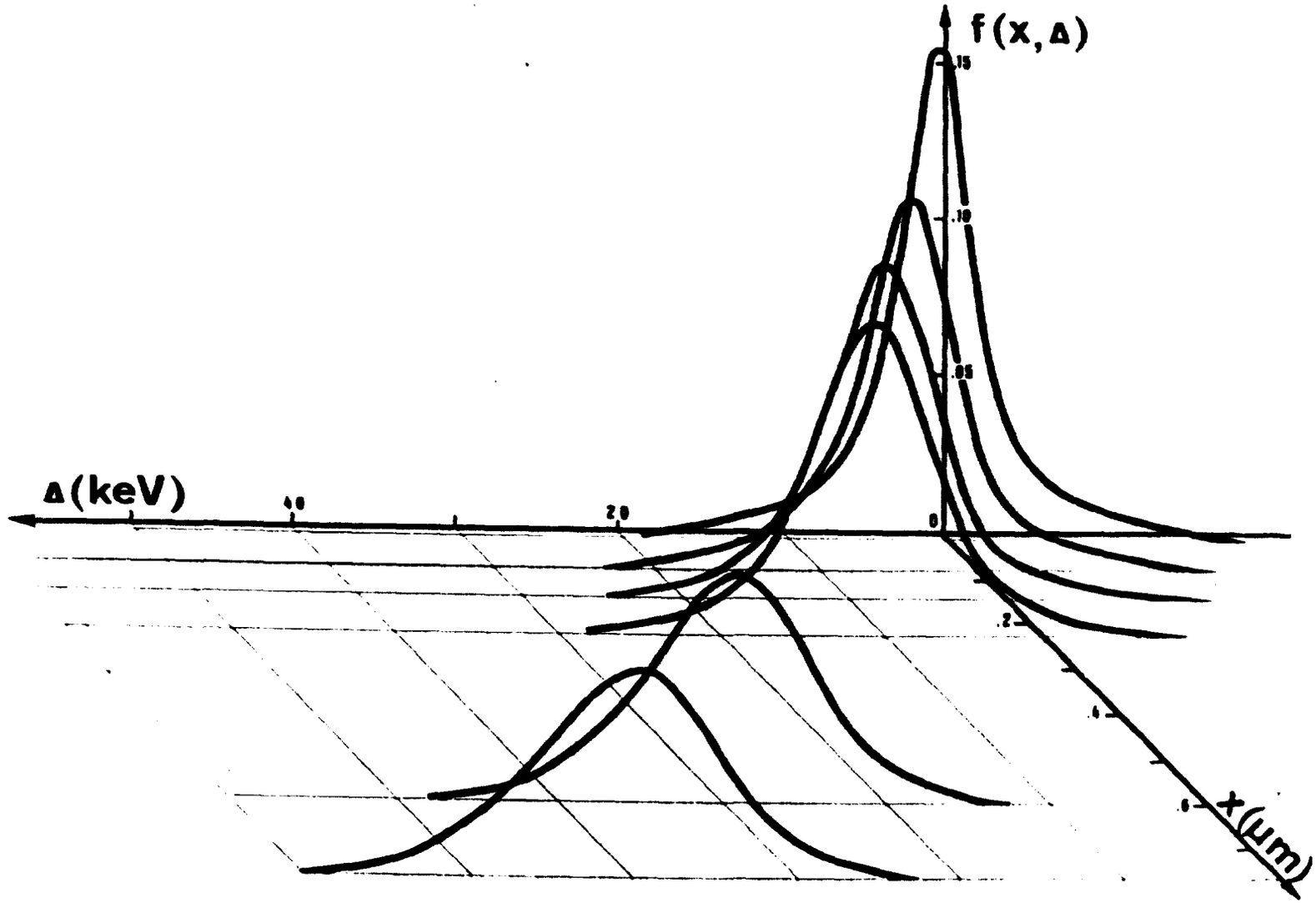

FIG. 7

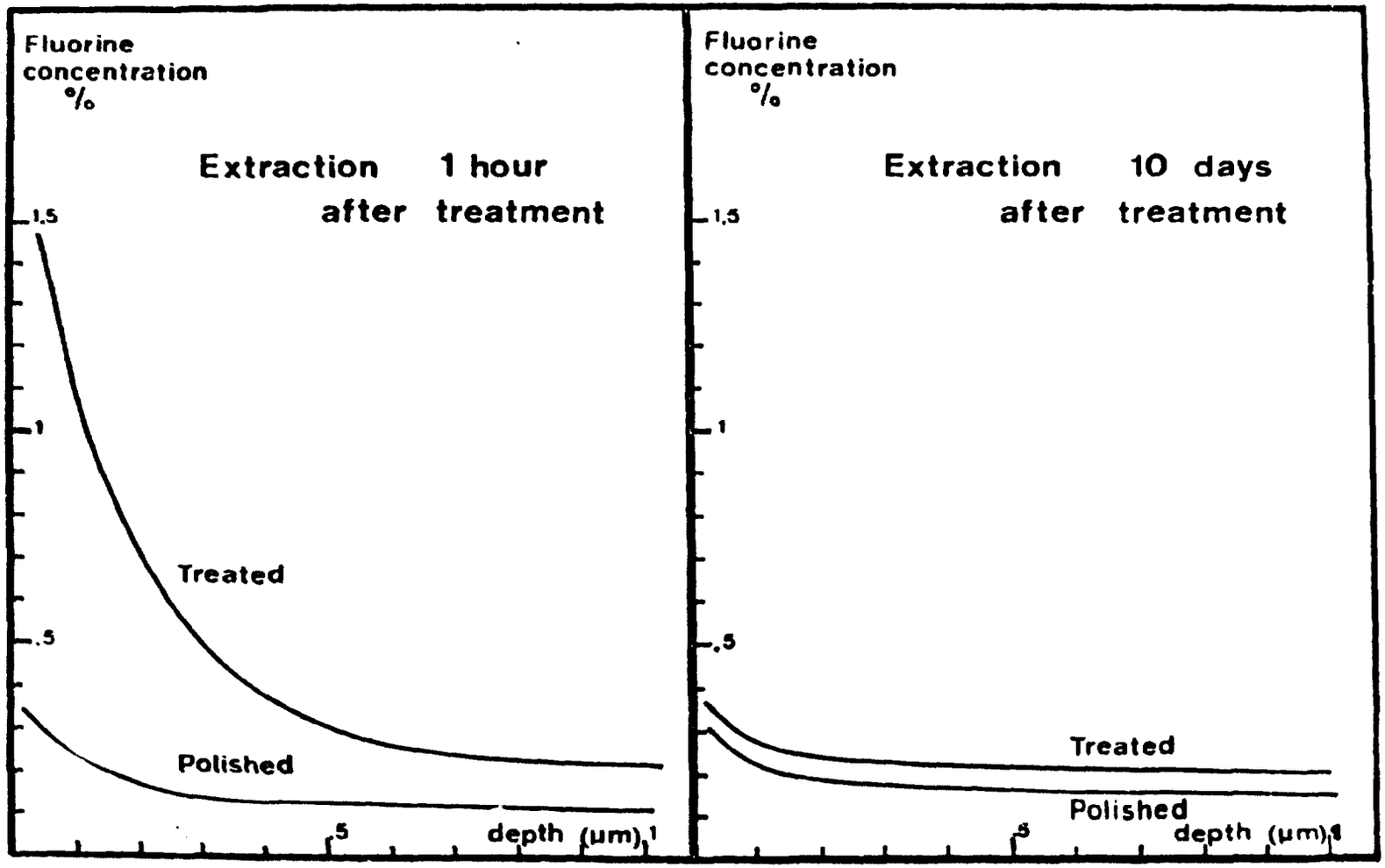
Fluorine concentration %
Extraction 1 hour after treatment
1,5
1
,5
Treated
Polished
,5
1
depth (µm)
Fluorine concentration %
Extraction 10 days after treatment
1,5
1
,5
Treated
Polished
,5
1
depth (µm)

FIG.8

FIG.9

REFERENCES.

1. E. MOLLER and N. STARFELT, Nucl. Inst. and Methods 50 (1967) 225.
2. J.W.MANDLER, R.B. MOLER, E. RAISEN and K.S. RAJAN. Thin Solid Films 19 (1973) 166-172.
3. I. GOLICHEFF, M. LOEUILLET and Ch. ENGELMAN. Journal of Radioanal. Chemistry, 12 (1972) 233-250.
4. G. DECONNINCK, Journal of Radional. Chem. 12 (1972) 157-159.
5. G. DECONNINCK and Y. FOUILHE. Rapport L.A.R.N. n° 755.