DECONTAMINATION OF FISSION PRODUCTS ON HUMAN SKIN AND HAIR

YASUSHI NISHIWAKI and HAJIME NISHIOKA
Department of Radiation Protection and Health Physics,
Research Laboratory of Nuclear Reactor,
Tokyo Institute of Technology, Tokyo, Japan

Abstract—The contamination and decontamination of human skin and hair may be influenced not only by the colloidal adsorption on the surface or absorption of radioactive substances into human tissue, but also by various physical, chemical and biological factors which make a reproducible decontamination experiment difficult. Therefore, in order to compare the efficiencies of various decontaminating agents we have employed a special device with which the conditions of decontamination could be kept more or less constant.

In these experiments, water, citric acid and the powerful chelating agents EDTA and DTPA were used for the purpose of decontamination of fission-products on a non-living, human skin sample and on hair. The decontaminated percentage (D_t), expressed in total gross activities, and the change of the decontaminated radioactivities per unit volume of eluting solution were measured.

Judged on the basis of the decontaminated percentage (D_t), the chelating agents were similarly effective in decontaminating the samples of human skin as with those of human hair. The radioactivities rapidly removed in the initial eluting solution seemed to indicate that there was a component that can be easily decontaminated with the chelating agents.

The persistently remaining activity appearing in the eluting solution after elution with 300–400 ml seemed to indicate that some of the strongly fixed or reacted component might have been gradually eluted out with the chelating agents. The decontaminated percentage (D_n) of each nuclide as estimated by the analysis of the γ-spectrum is given to show an order of magnitude.

The similarity in the mode of decontamination between the samples of human skin and those of hair may indicate, at least partly, the possibility of the existence of a competing effect of chelating agents against some of the reactions between metals in fission-products and proteins, for instance, keratin, collagen and so on which exist commonly in both samples.

Although it is anticipated that the use of chelating agents may enhance the absorption of some radioactive nuclides through the skin, if the solution containing the chelating agents were used for the decontamination of skin and hair in the form of a shower or by running water over the contaminated skin or hair to minimize the skin absorption, it may be extremely useful in some cases.

INTRODUCTION

With the increasing use of radioactive materials, the chances of radioactive contamination of the human body through the direct contact of the skin and the hair with radioactive substances may also increase. Since George *et al.*[1] reported the radioautographic studies on Pu-contaminated pig skin in 1956 and Khodyreva *et al.*[2] studied the internal permeability and transport into blood of Ra deposited on rabbit skin in 1959, many workers have studied radioactive contamination of the skin. As examples of using human skin as the experimental material, there have been such studies as the theoretical analysis of the behavior of Pu on the skin of the hand by Lister *et al.*[3] in 1963, the research on internal permeation of ^{22}Na and ^{131}I by Van Dilla *et al.*[4] in 1961, and the experiment of permeability of ^{90}Sr by Il'in[5] in 1960, and so on.[6-15]

These studies on skin contamination by various authors have been made with special attention to permeability or absorption of the radioactive ion into skin tissue. Therefore, it is natural that the studies of decontamination have also been done in relation to the skin permeability of the radioactive ion, for instance, as a function of the depth below the skin surface.

On the other hand, it has been observed that some of the biochemical substances existing in skin tissue, keratin or collagen, etc. may easily form a stable compound with metal ions.[16, 17] Therefore, it seems likely that the mechanism of contamination by radioactive metals on skin surface may be influenced not only by the phenomena of absorption or permeation of radioactive substances into tissue, but also by the colloidal adsorption and some reaction of the contaminant with the local tissue. In developing the method of decontamination of skin, we may have to take into consideration such a possibility.

In case of the contamination and decontamination of hair, there have been not so many studies in the past. However, this is an important problem, in view of the relatively large frequency of hair contamination. In this case also, the possible reaction between the radioactive contaminant and the biochemical substances in the hair such as protein, etc., may play an important role.

Judging from these points of views, it may be an effective decontamination method to use powerful chelating agents[18, 19] which have comparatively high abilities of chelate formation with a metal ion and compete with the conjugation between radioactive ions and protein, etc.

This study, although it is in a preliminary stage, was undertaken to estimate the chemical or biochemical significance of chelating agents at the time of decontamination of human skin and hair. With these purposes in mind, some chelating agents, citric acid, EDTA and DTPA which have various stability constants, were used for this decontamination experiment.

MATERIAL AND METHOD

1. *Human Skin Sample*

Sample materials used in this experiment were the human skin supplied by the Tokyo Metropolitan Medical Examiner's Office. The skin of size about 3 × 15 cm with subcutaneous fat was cut from the central part of the breast of a Japanese adult at about 10 hr after accidental death. At about 1 hr after sampling, the fat was removed and the skin was cut into squares, 3 × 3 cm. No pathological change was observed macroscopically at this stage. The skin sample was spread on a glass plate (4 × 4 cm) and fixed at four corners by Scotch tape, the back side of the skin facing the glass plate. As pretreatment, the skin surface, after having been slightly wiped with absorbent cotton soaked in 0.01 wt% DBS (dodecyl benzene sulfonate) solution, was cleaned several times with absorbent cotton soaked in water and then the excess moisture was absorbed off lightly by blotting with filter paper. The skin sample was contaminated with fission products solution (adjusted to pH 6.8 about 100 days after production) by micropipette and dried for one hour at room temperature. Gross activities T_0 of the contaminated samples were measured prior to decontamination by GM counter (SA-230, Kobe Kogyo). After the contaminated samples were

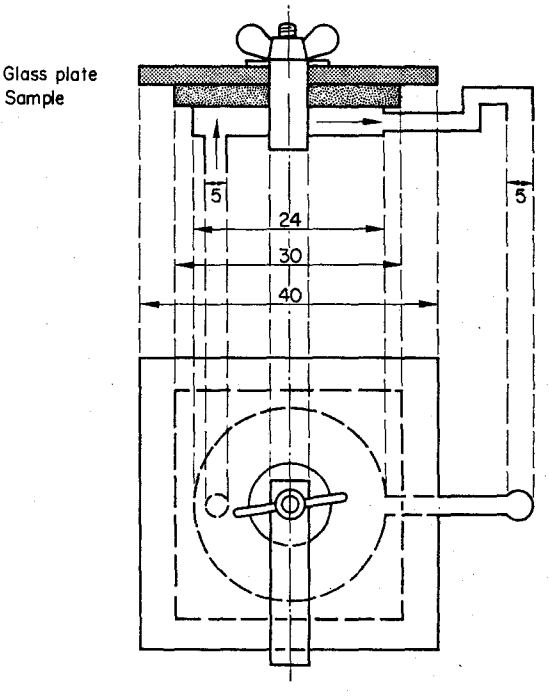

FIG. 1. Experimental apparatus for decontamination of fission products on human skin (mm).

set in the experimental apparatus as shown in Fig. 1, the skin was decontaminated by flowing water, citric acid, EDTA or DTPA solution (0.01 m/l.)[20, 21] at the rate of 6 ml/min, and 1 ml of the eluting solution was collected successively at intervals into sample cells. The radioactivities of these samples after drying on a hot plate were measured by use of a 2π gas flow, low background GM counter (SC-5, Aloka). The temperature of the flowing solution was about 20°C. After having flowed a total volume of 1 l. of decontaminating water or the solutions, these sample materials were taken out from the apparatus. After drying the sample, the gross activities T_1 of the sample after decontamination were measured. The γ-ray spectra of these contaminated samples were also taken before and after decontamination with a 256 channel pulse height analyser. For this analysis a NaI (Tl) crystal of diameter 3 in. and length 3 in. was used. The distance between samples and detector was about 5 mm.

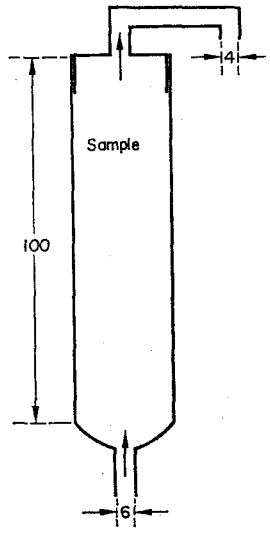

FIG. 2. Experimental apparatus for decontamination of fission products on hair (mm).

2. *Human Hair Sample*

Sample materials used were hair of several Japanese men 18–22 years old which were collected at a barber shop. They had a diameter of about 0.1–0.2 mm and length about 8–15 cm. As pretreatment, the samples were immersed and stirred in 0.01 wt% DBS solution for 30 min in order to remove the adsorbed dust, organic substances, etc. After washing with 5 l. of water, the samples were dried at room temperature on filter paper for about 2 hr. Then, 4 g of these sample materials were put in a gauze bag of diameter about 2.5 cm and length about 10 cm. These bags, containing 4 g, were immersed in the solution of fission products in the same way as in experiment 1, so that the solution contacted the sample hair homogeneously. After having been taken out from the solution of fission products, these samples were dried for 4 hr at room temperature on filter paper. After measuring the gross activities T_0 of the contaminated samples prior to decontamination, they were set in a cylindrical column made of glass as shown in Fig. 2. The contaminated samples were decontaminated by flowing water and decontaminating solution through the column and the radioactivity eluted into water or into the solution of citric acid, EDTA or DTPA was measured as in experiment 1. After measuring the gross activities T_1 of the sample after decontamination, the samples in the bag were transferred into the tube made by polystyrol with the same size as the column and the γ-ray spectrum was taken. When measuring the γ-ray spectrum, the detector was placed as close to the side of the polystyrol tube as possible.

RESULTS

From the gross activities T_0 and T_1, decontaminated per cents, D_t, of the samples of human skin and hair were calculated. The results are shown in Table 1. D_t was calculated by the following equation.

$$D_t = \left(1 - \frac{T_1}{T_0}\right) \times 100$$

Figure 3 for human skin and Fig. 4 for hair show the relation of the gross activity cpm/ml and the volume of the eluting solution. One ml was sampled at the beginning of the elution and thereafter 1 ml every 10 ml of elution up to the initial 100 ml; from 100 ml to 500 ml of elution, 1 ml every 20 ml; from 500 to 1000 ml of elution, 1 ml every 50 ml; Each aliquot of the sampled solution was measured for gross activity. In Fig. 5 for human skin and in Fig. 6 for hair,

Table 1. Gross Activities of Fission Products before and after decontamination of Contaminated Human Skin and Hair and Decontaminated Percentage (D_t)

	Decontamination agents	Before decontamination T_0 (cpm)	After decontamination T_1 (cpm)	Decontaminated percentage D_t $\left(1-\frac{T_1}{T_0}\right)\times 100$
Skin	Water	8.36×10^3	7.96×10^3	5
	Citric acid	7.96×10^3	5.14×10^3	35
	EDTA	8.60×10^3	2.91×10^3	66
	DTPA	8.94×10^3	3.67×10^3	59
Hair	Water	1.22×10^4	1.18×10^4	3
	Citric acid	1.08×10^4	6.50×10^3	40
	EDTA	1.14×10^4	3.95×10^3	74
	DTPA	1.22×10^4	4.25×10^3	65

γ-ray spectra of the contaminated sample prior to decontamination and that of the samples after decontamination by water, citric acid, EDTA or DTPA solution are shown as an example. The data concerning the possible radionuclides corresponding to the clear peaks in these spectra are shown in Table 2. The possible corresponding nuclides are ^{141}Ce, ^{144}Ce, ^{103}Ru, ^{95}Zr, ^{95}Nb, ^{91}Y and ^{140}La as listed in Table 2.

The peak area of each corresponding nuclide

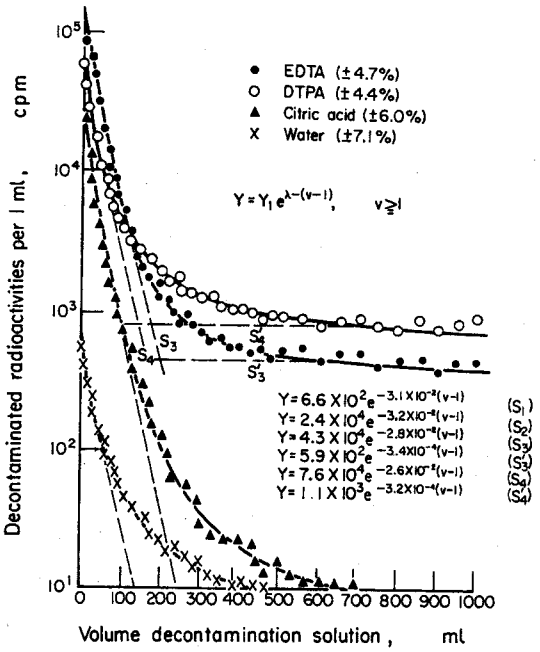

FIG. 3. Decontamination rate of fission products on human skin.

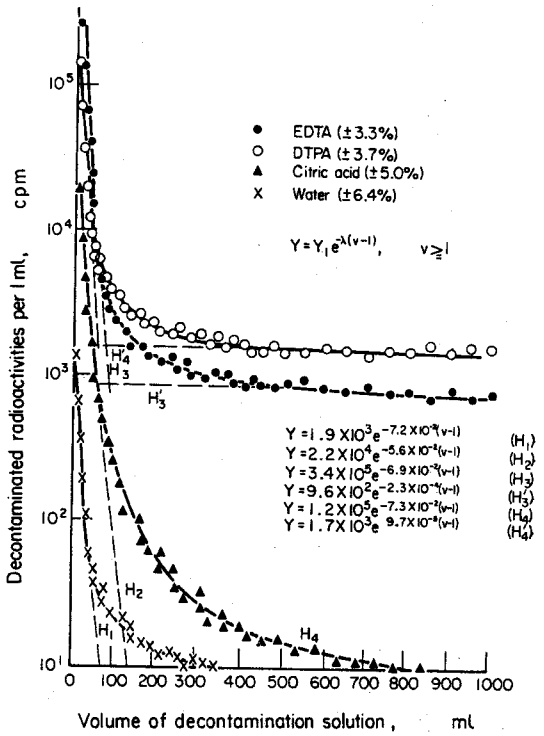

FIG. 4. Decontamination rate of fission products on hair.

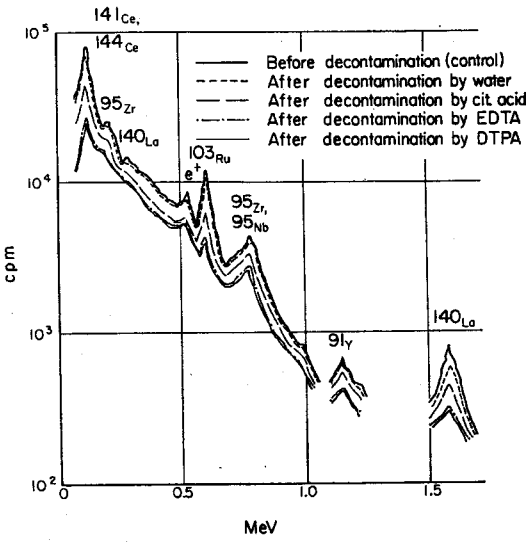

FIG. 5. γ-ray spectra before and after decontamination of skin contaminated with fission products.

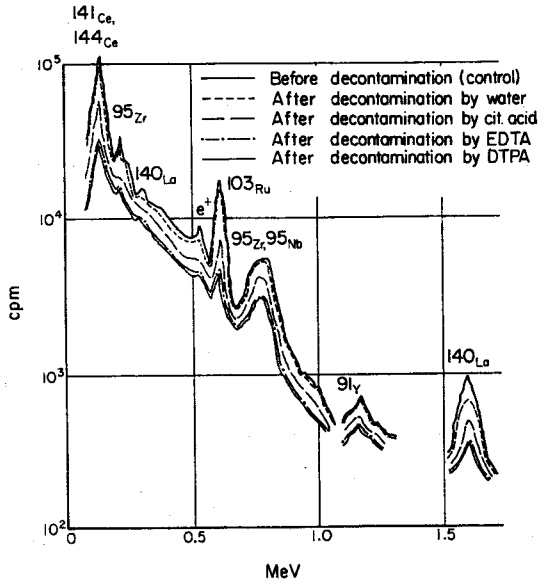

FIG. 6. γ-ray spectra before and after decontamination of hair contaminated with fission products.

was obtained by Covell's method,[232] and the decontaminated percentage D_n of each nuclide calculated from the peak area count N_0 and N_1 are shown in Table 3[23] for human skin and in Table 4 for hair. D_n was calculated as follows,

$$D_n = \left(1 - \frac{N_1}{N_0}\right) \times 100$$

where N_0 is the activity of the contaminated sample prior to decontamination and N_1 that of the sample after decontamination.

DISCUSSION

For the effective decontamination of the radioactive contamination on human skin and hair,

Table 2. γ-Spectrum Assaying Data for Fission Products used in these Experiments

Spectrum peak (MeV)	Corresponding nuclide	γ-ray energy (MeV)	Abundance in fission products at 150 days[22]	Traced peak
0.13	^{144}Ce ^{141}Ce	0.134 0.145	0.97 0.45	O
0.22	^{95}Zr	0.235	1.55	
0.33	^{140}La	0.328	f	
0.51	e^+	0.51		
0.62	^{103}Ru	0.61	0.55	O
0.75	^{95}Zr ^{95}Nb	0.725 0.75 0.768	1.55 2.40	O
1.15	^{91}Y	1.19	1.25	O
1.61	^{140}La	1.60	f	O

f: a trace amount.

Table 3. Decontaminated Percentage of Each Traced Nuclide in Fission Products on Skin

Traced nuclide	Decontamination agents	Decontaminated percentage D_n* $\left(1+\frac{N_1}{N_0}\right)\times 100$
^{141}Ce, ^{144}Ce	Water	2
	Citric acid	28
	EDTA	47
	DTPA	48
^{103}Ru	Water	10
	Citric acid	34
	EDTA	46
	DTPA	46
^{95}Zr, ^{95}Nb	Water	4
	Citric acid	22
	EDTA	45
	DTPA	39
^{91}Y	Water	5
	Citric acid	25
	EDTA	52
	DTPA	44
^{104}La	Water	24
	Citric acid	40
	EDTA	57
	DTPA	60

* These figures should be interpreted to show only an order of magnitude estimate, because of the difficulty of exactly reproducible experiments.

it may be necessary to clarify the contamination mechanism on these surfaces.

In the actual contamination of mixed fission products it is very difficult to understand the mechanism because of the multiple complex factors involved in contamination and reproducible experiments are usually very difficult. Therefore, in order to compare the efficiences of various decontaminating agents we have employed a special device so that the conditions of decontamination could be kept more or less constant, as shown in Figs. 1 and 2.

Judging from our experimental results, the percentage of free contamination that can be removed easily even by water alone seems to be quite large. Therefore, in our cases of the contamination of biological surfaces, the percentage of fixed or reacted contamination appeared to be relatively small, although there may be some biologically reactive substances included in the skin tissues. However, depending upon the mode of contamination and the physical-chemical state of the contaminant, the reacted contamination may not be considered negligible. Especially, in case of heavy contamination, even though the percentage of the fixed or reacted contamination is small, the residual fixed contamination that cannot be easily

Table 4. Decontaminated Percentage of Each Traced Nuclide in Fission Products on Hair

Traced nuclide	Decontamination agents	Decontaminated percentage D_n* $\left(1+\frac{N_1}{N_0}\right)\times 100$
^{141}Ce, ^{144}Ce	Water	4
	Citric acid	31
	EDTA	45
	DTPA	52
^{103}Ru	Water	9
	Citric acid	35
	EDTA	51
	DTPA	52
^{65}Zr, ^{95}Nb	Water	1
	Citric acid	24
	EDTA	43
	DTPA	42
^{91}Y	Water	2
	Citric acid	26
	EDTA	53
	DTPA	46
^{103}La	Water	26
	Citric acid	46
	EDTA	55
	DTPA	59

* These figures should be interpreted to show only an order of magnitude estimate, because of the difficulty of exactly reproducible experiments.

removed by water alone may play an important role.

In these experiments, a fission product mixture, which is one of the most important contaminants at the time of a reactor accident, was used. On the other hand, as the materials to be contaminated, human skin and hair were used.

Table 1 shows the gross activity of the fission product mixture on human skin and hair before and after decontamination as well as the decontamination percentage. As can be seen in Table 1 the difference of decontamination effect between water, citric acid and the strong chelating agents (EDTA, DTPA) was clearly observed. The highest decontamination effect was observed with EDTA and DTPA and the lowest with water alone. Citric acid showed an intermediate efficiency. These tendencies were observed both for human skin and human hair. These differences in the decontamination efficiency may be ascribed to the difference in the stability constant of the decontaminating agents with some of the metal ions in the fission product mixture. The strong chelating agents such as EDTA and DTPA with a high stability constant may remove some of the metal ions of the fission products competitively from some of the

less reactive biological substances with a smaller stability constant included in the skin and hair tissues. The eluted radioactivity per unit volume of elution as a function of the volume of eluting decontamination solution is shown in Fig. 3 for human skin and in Fig. 4 for human hair on a semi-logarithmic scale. Although these experiments were conducted at the elution rate of 6 ml/min and at room temperature (about 20°C), it is very likely that the results may be influenced by the flow rate and the composition of the decontaminating solutions, the temperature at the time of decontamination and other various physical, chemical and biological factors which may affect the state of contamination. As can be seen in these figures, tangent lines were drawn along the linear part of the decontamination rate curves on the semi-logarithmic plot. These lines are designated as S_1, S_2, S_3, S_3', S_4 and S_4' in case of human skin and by H_1, H_2, H_3, H_3', H_4, and H_4' in case of human hair. They may be approximately expressed by the following empirical formula,

$$Y = Y_1 e^{-\lambda(v-1)}, \qquad (v \geq 1)$$

where Y is the decontaminated activity per unit volume (1 ml) of decontaminating solution, Y_1 the initial decontaminated activity into the initial unit volume (1 ml) of decontaminating solution, v the volume of eluting decontamination solution expressed in ml, and λ the decontamination constant.

The values of the initial decontaminated activity Y_1 and the decontamination constant λ are listed in Table 5. As can be seen in the table, the values of the decontamination rate constant λ for the initial part of the decontamination are almost the same. They are roughly about 0.03 in the case of human skin and about 0.06–0.07 in the case of human hair under the conditions of our experiment. However, considerable differences were observed in the initial decontaminated activity Y_1 for water alone and for the different chelating agents. In the case of human skin, the decontamination rate constant λ after about 300 ml of elution with EDTA and DTPA is observed to decrease down to about 1/100 as compared with the initial part, while in the case of human hair the value of λ after about 200 ml of elution with EDTA and DTPA decreases down to about 1/300–1/700. Although the initial decontaminated activity is much higher with citric acid than with water alone, the overall shapes of the decontamination rate curves are similar for both citric acid and water alone, and are quite different from those of EDTA and DTPA. In case of citric acid and water alone, the decontaminated radioactivity

Table 5. The Values of the Initial Decontaminated Activity Y_1 and the Decontamination Constant λ ($Y = Y_1 e^{-\lambda(v-1)}$).

Samples	Decontamination agents	Y_1	λ
Human skin	Water (S_1)	6.6×10^3	3.1×10^{-2}
	Citric acid (S_2)	2.4×10^4	3.2×10^{-2}
	EDTA (S_3)	4.3×10^4	2.8×10^{-2}
	(S_3')	5.9×10^3	3.4×10^{-4}
	DTPA (S_4)	7.6×10^4	2.6×10^{-2}
	(S_4')	1.1×10^3	3.2×10^{-4}
Human hair	Water (H_1)	1.9×10^3	7.2×10^{-2}
	Citric acid (H_2)	2.2×10^4	5.6×10^{-2}
	EDTA (H_3)	3.4×10^5	6.9×10^{-2}
	(H_3')	9.6×10^3	2.3×10^{-4}
	DTPA (H_4)	1.2×10^5	7.3×10^{-2}
	(H_4')	1.7×10^3	9.7×10^{-5}

per unit volume of elution decreased down close to the natural background level after about 200–300 ml of elution, which seems to indicate that no more appreciable decontamination is available thereafter. The stability constants of citric acid are lower than that of EDTA and DTPA for most of the metals. In case of the strong chelating agents EDTA and DTPA with high stability constants with some of the metals, although the rate of decontamination decreases greatly after about 200–300 ml of elution as can be seen in the decrease of λ, the elution of a considerable activity was observed to continue until the total volume (1000 ml) of decontaminating solution available for our experiments was used.

Some of the γ-ray spectra of fission products taken before and after decontamination are shown in Fig. 5 for human skin and in Fig. 6 for hair. In these spectra the peaks corresponding to the nuclides ^{144}Ce, ^{141}Ce, ^{95}Zr, ^{140}La, ^{90}Y, ^{103}Ru were traced as shown in Table 2. The peak areas of the peaks corresponding to the traced nuclides were calculated by Covell's method and the decontaminated percentage of each corresponding nuclide was estimated. These values are shown in Table 3 for human skin and in Table 4 for hair. Although they should be interpreted to show only an order of magnitude, it is clear that the decontamination effect of the chelating agents is remarkably better than that of the water alone.

However, because of the possible existence of various decay chains in the fission product mixture, in order to obtain more precise results a more detailed time analysis of the γ-spectra and radiochemical analysis may be necessary. In our experiment, we have taken several γ-spectra, but in cases where there is a possibility of the parent and daughter nuclides separating out, we must be extremely cautious about the interpretation of the γ-spectra.

Although some minor differences were observed in the decontamination effect on human skin and hair, overall similarity was observed in the effects and modes of decontamination for skin and hair under the conditions of our experiments. In either case, the strong chelating agents EDTA and DTPA with high stability constants with metal ions seem to be effective decontaminating agents for fission product mixture.

If the solution containing the chelating agents were used for the decontamination of skin surfaces in the form of a stagnant bath, it may be anticipated that the chelating agents may enhance the absorption of some radioactive nuclides through the skin surfaces.

However, if the chelating agents were used for the decontamination of skin and hair in the form of a shower or by running water over skin and hair to minimize the skin absorption, it may be extremely useful in some cases of skin and hair contamination.

REFERENCES

1. L. A. George, Jr., N. L. Dockum and L. K. Bustad. Decontamination of pig skin contaminated with a plutonium solution. Hanford Report HW-44526, 1956.
2. M. A. Khodyreva. The permeability of radium bromide through intact skin. *Med. Radiol.* **4,** 77–81 (1959).
3. B. A. J. Lister, A. Morgan and R. S. Sherwood. Excretion of plutonium following accidental skin contamination. *Health Physics* **9,** 80–915 (1963).
4. M. A. Van Dilla, C. R. Richmond and J. E. Furchner. Cutaneous absorption by human subjects. 1. Studies with sodium-24 and iodine-131. LAMS-2526, 1961.
5. L. A. Il'in. Contamination of the skin by radioactive substances and comparative effectiveness of certain methods of purification. *Gigiena Truda i Professional Zabolezaniya* **4,** 28–32 (1960).
6. W. J. Friedman. Decontamination of synthetic radioactive fallout from the intact human skin. *Am. Ind. Hyg. Ass. J.* **19,** 15–19 (1958).
7. J. Nosek and V. Chmelar. On the present possibilities of washing radioactive substances off the skin of living animals. *Health Physics* **2,** 306–307 (1960).
8. M. H. Weeks and W. D. Oakley. Biology research—annual report for 1953–1954. Hanford Report HW-30437: 102–110, 1954. Ibid. HW-35917: 59–64, 1955.
9. L. A. George, Jr., N. L. Dockum and L. A. Bustad. Biology research—annual report for 1956. Ibid. HW-47500: 147–156, 1956.
10. W. D. Oakley and R. C. Thompson. Biology research—annual report for 1955. Ibid. HW-41500: 106–122, 1955.
11. F. P. Hungate and E. G. Swedea. Biology research—annual report for 1961. Ibid. HW-69500: 111–135, 1961.
12. R. H. Wilson and W. B. Silker. Plutonium contaminated injury case study and associated

use of Na_2 EDTA as a decontamination agent. Ibid. HW-55309: 5–6, 1960.
13. Y. Nosek and V. Khmelarzh. Skin disactivation in contamination with radioactive substances. *Med. Radiol.* **4,** 74–76 (1959).
14. J. Toulet and J. Tabernat. Contribution to the study of processes for external decontamination experimentation with a new product in the case of radioactive contamination of the teguments. *Arch. Maladies Profess. Med. Travail et Securite Sociale* **20,** 272–282 (1959).
15. M. H. Faes. Skin decontamination in presence of thallium-204. *Nature* **194,** 1188–1189 (1962).
16. I. M. Klotz. The conjugation between protein and micromolecule ion or micromolecule compound. *Protein Chemistry* **4,** 15–63 (1956).
17. H. Noda. Collagen. *Protein Chemistry* **4,** 65–125 (1956).
18. A. E. Martell and M. Calvin. *Chemistry of the Metal Chelate Compounds,* p. 454, Prentice Hall, New York, (1952).
19. Y. Nishiwaki and H. Nishioka. The method of decontamination of radioactive surface contamination (The effect of surfactants and chelating agents). *Bull. of Tokyo Institute of Technology* **54,** 131–136 (1963).
20. Y. Nishiwaki and H. Nishioka. On the removal of the radioactive surface contaminations. Ibid. **61,** 13–28 (1964).
21. H. Nishioka. The mechanism of radioactive surface contamination and decontaminating agents **1,** II. *Industrial Environmental Engineering* **30,** 2–9 (1964). Ibid. **31,** 1–8 (1964).
22. H. F. Hunter and N. E. Ballou. Fission-products decay rates. *Nucleonics* **9,** C.2–C.7 (1951).
23. D. F. Covell. Determination of gamma-ray abundance directly from the total absorption peak. *Anal. Chem.* **31,** 1785–1790 (1959).