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LEACHING OF URANIUM FROM GLASS AND CERAMIC FOODWARE AND DECORATIVE ITEMS

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Abstract—Beginning as early as the first century A. D. and continuing until at least the 1970s, uranium was used as a coloring agent in glass and in ceramic glazes. The leaching of uranium from such items is of interest as some were designed for food storage or serving. Thirty-three glass items and two ceramic items were leached sequentially with deionized water, dilute acetic acid, and 1 M nitric acid to assess realistic and worst-case scenario leaching by foods and beverages. The maximum quantity of uranium leached from the uranium-bearing glasses was about $30 \mu\text{g L}^{-1}$, while that from the ceramic-glazed items was about $300,000 \mu\text{g L}^{-1}$. *Health Phys.* 63(3):343–348; 1992

Key words: uranium; ingestion; intake, radionuclide; nutrition pathways

INTRODUCTION

GRAZIANO and Blum (1991) recently reported on the leaching of lead from lead crystal decanters and drinking glasses and the associated health implications. They showed increases in the lead concentration of wines and spirits in contact with lead crystal vessels in both short-term (i.e., minutes) and long-term (i.e., months) experiments. This report, and the subsequent Food and Drug Administration warning (Food and Drug Administration 1991) prompted our interest in leachable uranium from uranium-containing glass.

Today, uranium-bearing glasses (containing about 0.5 to 1% UO_2) are prepared at nuclear research facilities to study the use of glass as a matrix for the containment and disposal of high-level radioactive waste (Ebert and Bates 1990). However, uranium-containing glasses are not solely a recent product; indeed, their history dates to antiquity.

History of uranium-containing glassware and ceramic glazes

A sample of pale yellow-green glass from a first-century A. D. mosaic mural in the Imperial Roman Villa near Naples, excavated around 1910 by Oxford University archaeologists, was found to contain about

1% uranium. The uranium is thought to have been added intentionally by the Roman artisans, in the form of a uranium-bearing mineral, to impart color to the glass. Commercial applications of uranium during the 19th and early 20th centuries were limited and focused on the use of uranium salts as coloring agents in ceramic glazes and ornamental glass.

During the early 20th century, uranium salts were produced as by-products of the radium extraction industry. Yellow sodium uranate was used in quantities of up to 25 weight-percent to produce a green-yellow glass referred to as "canary" or "vaseline" glass (Landa 1987). Both "canary" and "vaseline" refer to the yellow color of the glass. The latter term is somewhat puzzling as the color of the glass does not resemble today's petroleum jelly. Probably in an attempt to rationalize the term with the observable properties of the glass, some antique dealers state that the "vaseline" descriptor denotes an unusually slippery feel that they allege this variety of glass to possess. It is more likely that the true origin of the term is related to the appearance of petroleum jelly in earlier years, when the decolorizing steps in the manufacturing process were less stringent than in recent times (Landa 1987). While some items were strictly decorative, many were designed for the serving and storage of food (e.g., plates, cups, and jugs).

Usage of uranium salts as a coloring agent in glasses and ceramic glazes increased during the late 1920s and the 1930s in the United States. U.S. Bureau of Mines statistics showed the importation of uranium salts during 1928–1938 to be between 70,000 and 170,000 kg y^{-1} (Landa 1987). As development of the atomic bomb moved forward, the U.S. War Production Board issued an order in January 1943 that largely prohibited the use of uranium for nonmilitary purposes. As a result, the use of uranium salts in the ceramics industry fell to 3,400 kg in 1943, and to 50 kg in 1944. Substitute coloring compounds, including an antimony-iron material, were soon being used in ceramic glazes.

When restrictions were lifted in 1959, the use of uranium salts began again, largely for dinnerware, with

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¹ Personal communication (1991), E. Henrich, Austrian Ministry of Health (BMGSK), Vienna. In German-speaking countries, the uranium-bearing glass is referred to as "Anna glass," a collection of which can be seen at the Thurn Museum in Thurn, Germany (von Philipsborn 1988). Two varieties are distinguished—a green (annagrün) and a yellow (annagelb).

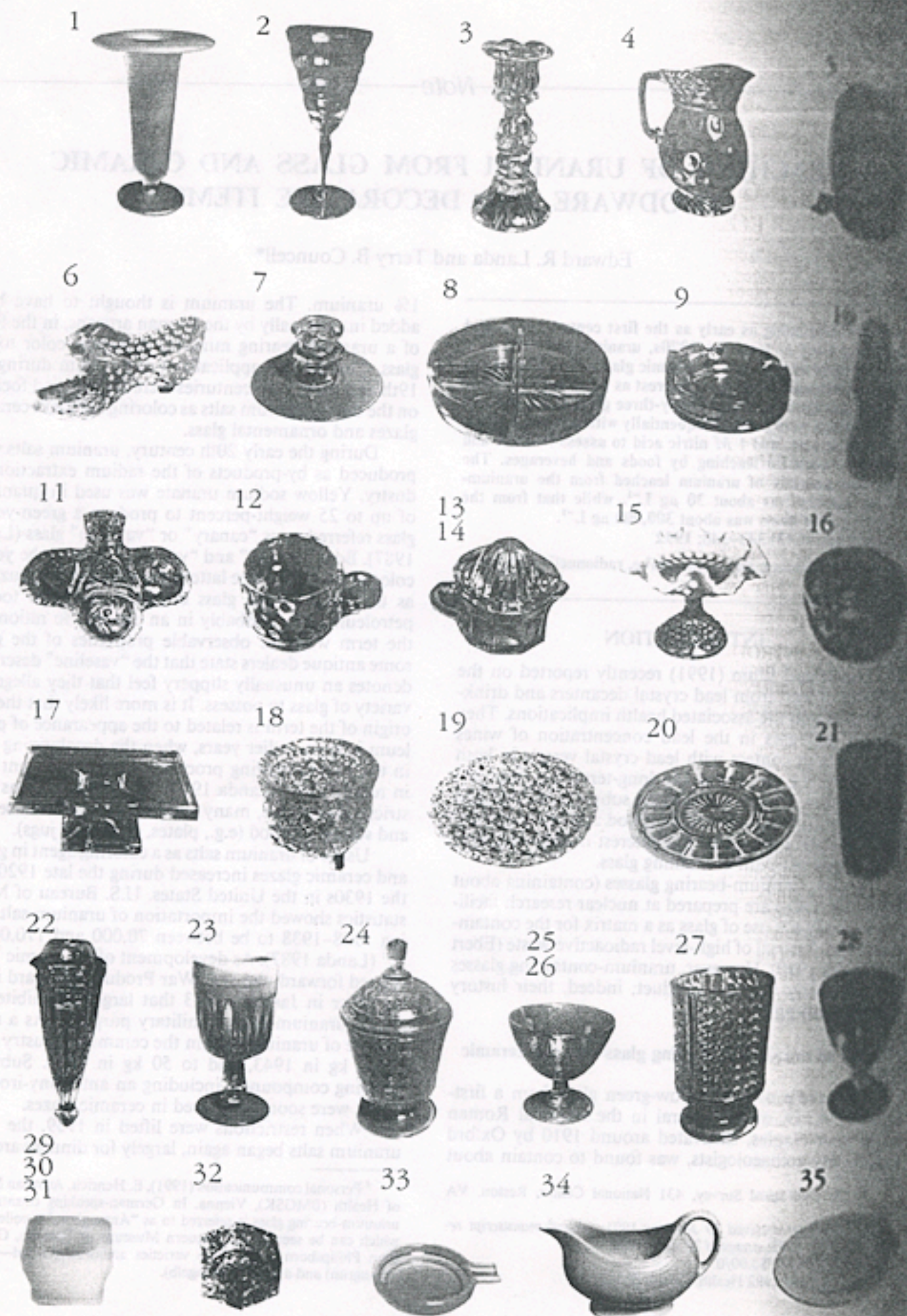


Fig. 1. Glass and ceramic items tested. The glass items (samples 1-33) were all yellow-green. The Flinstan items (samples 34-35) were red-orange. (Items with more than one number are part of a set.)

a red-orange glaze. The production of the major variety ("Fiesta")² of uranium-glazed tableware ended in 1972 (Landa 1987). McCormick (1992) has monitored an assortment of Fiesta ware bowls, pitchers, and plates with an ion chamber and reports exposures of $5.2\text{--}26 \times 10^{-7} \text{ C kg}^{-1} \text{ h}^{-1}$ ($2\text{--}10 \text{ mR h}^{-1}$). While not a major health hazard, the culinary use of such items in recent years has been discouraged by public health officials, in line with other measures designed to eliminate or reduce unnecessary and avoidable radiation exposure to the public (U.S. Environmental Protection Agency (EPA) 1977; Brown 1981). The glass and ceramic pieces are now regarded as collectible and are frequently seen in antique shops. However, few consumers are probably aware of their uranium content.

The radioactive character of red Fiesta glazes received considerable attention in the 21 October 1991 issue of *The New Yorker* magazine (Schuyler 1991). Also, a not-to-be-missed radiograph made using an orange dinner plate with a uranium-bearing glaze appears in the November 1991 issue of the Radiological Society of North America's pictorial journal, *RadioGraphics* (Sirr 1991). Steven A. Sirr of the Department of Radiology, Abbott Northwestern Hospital, Minneapolis, MN, positioned a teaching skeletal hand and a metallic table fork atop the plate, and produced an image of the hand and fork during a 7-d exposure of a film using the plate as the source of radiation. That same issue of *RadioGraphics* contains a scintigram of a Fiesta ware dessert dish made with a sodium iodide nuclear medicine camera by Nick Hesselman and David DiSantis of the Department of Radiology, DePaul Medical Center, Norfolk, VA (DiSantis and DiSantis 1991).

Comparing lead- and uranium-containing glassware and ceramic glazes

As a point of comparison of the relative toxicity of lead and uranium, the EPA maximum allowable level of lead in drinking water is $50 \mu\text{g L}^{-1}$; this value will probably be revised to $20 \mu\text{g L}^{-1}$ (Graziano and Blum 1991). The presently proposed EPA regulations for radionuclides in drinking water would establish a maximum contaminant level for uranium of $20 \mu\text{g L}^{-1}$ (U.S. EPA 1991a). The health hazards associated with uranium stem from both its chemical toxicity, resulting in damage to the proximal convoluted tubules of the kidneys, and its radiation effects and carcinogenicity (U.S. EPA 1991b). The adverse health effects associated with lead include gout, hypertension, renal changes, altered erythropoiesis, nervous-system disorders, and deficits in cognitive function after *in-utero* exposure (Graziano and Blum 1991).

Our testing was done to estimate the intake of uranium by persons using uranium-bearing glass and ceramic items for food storage and serving. Non-foodware glass items such as ash trays and candlestick

holders were tested to increase the range of glass compositions examined on the assumption that, in the past when such glassware was being produced, these same glasses might just as well have been cast into foodware items as into decorative items.

MATERIALS AND METHODS

The glass and ceramic items studied (Fig. 1; Table 1) came from the private collection of the first author. They were washed in laboratory detergent and thoroughly rinsed with deionized water prior to testing. A sequential leaching scheme was used:

- (1) deionized water;
- (2) 4% (volume/volume) acetic acid; and
- (3) 1 M nitric acid.

Twenty milliliters of solution was used and the tests were done at room temperature. Items were covered with watchglasses, Parafilm,³ or a sealing beaker to prevent evaporation during the test period. The contact time for each solution was 24 h. The leachant was added to the liquid- or food-receiving surface of the foodware items, or to cavities in the non-foodware items. Where a cavity $>20 \text{ cm}^3$ did not exist, the items were immersed in 20 mL of the leachant. The items were rinsed with deionized water between steps 2 and 3. The deionized-water leachate solutions of step 1 were adjusted to 1 M with respect to HNO_3 by the addition of concentrated acid for sample preservation at the end of the 24-h time period and after transfer of the sample to a polyethylene vial. The leachate was analyzed for uranium with a kinetic phosphorescence analyzer.⁴

Because all these items have attained the status of antiques, destructive testing to ascertain uranium content was deemed undesirable. However, for the purposes of this study, it was important to know that the glass tested was indeed colored by the addition of a uranium salt and not by some other substance(s) that might render it yellow-green.

The fluorescence of some uranium minerals under ultraviolet (UV) light has been used in prospecting for uranium ores and in analytical procedures for uranium in aqueous samples. When examined under either a short wavelength (254 nm) or long wavelength (365 nm) UV lamp,⁵ all of the glass pieces except sample 28 exhibited fluorescence. Each glass or ceramic sample was then placed above a $7.6 \times 7.6\text{-cm}$ NaI(Tl) crystal and counted for 1 h using a single-channel analyzer with a wide-open window. As can be seen from the photographs in Fig. 1, the sample geometry was ob-

² Use of brand names and firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

³ American Can Company, 8770 West Bryn Mawr Ave., Suite 06B, Chicago, IL 60631.

⁴ Chemchek Instruments, Inc., Model KPA-10, 1845 Terminal Drive, Richland, WA 99352.

⁵ UVP, Inc., Models H4-5 and H4-L, 5100 Walnut Grove Ave., San Gabriel, CA 91778.

¹ Homer Laughlin China Co., 6th and Harrison St., Newell, WV 26050.

Table 1. Sample characteristics and leaching results with water (H_2O), 4% acetic acid (CH_3COOH), and 1 M nitric acid (HNO_3).

Sample number	Description	Weight (g)	Radioassay (net counts h ⁻¹ g ⁻¹)	Uranium leachate assay (μg L ⁻¹)		
				H ₂ O	CH ₃ COOH	HNO ₃
<i>Glass</i>						
1	Vase, frosted	503	740	0.06	30.1	29.7
2	Long-stemmed wine glass	116	333	<LLD*	<LLD	1.9
3	Tall candlestick holder	425	74	<LLD	<LLD	0.3
4	Pitcher	711	173	<LLD	<LLD	4.7
5	Beverage crock	980	295	0.07	3.7	0.0
6	Decorative glass slipper	249	364	<LLD	7.2	4.1
7	Low-form candlestick holder	241	1,727	0.03	7.3	22.3
8	Circular, sectioned candy dish	1,087	164	<LLD	3.5	4.3
9	Large ashtray	592	367	0.22	12.1	10.5
10	Salt shaker	108	320	0.63	5.2	1.9
11	Clover-shaped candy dish	289	486	0.05	11.0	28.8
12	Cup with handle	162	243	<LLD	19.8	1.5
13	Juice squeezer (receptacle)	214	840	0.08	9.1	2.8
14	Juice squeezer (top)	197	918	0.28	5.5	7.5
15	Candy dish with hobnail base	835	323	0.16	2.5	2.9
16	Small bowl	242	301	<LLD	0.6	1.4
17	Chewing gum display stand	637	432	<LLD	3.0	8.7
18	Three-legged bowl	175	171	<LLD	—	1.4
19	Cut-glass plate	176	422	0.22	15.0	9.1
20	Plate	265	609	<LLD	0.5	2.8
21	Drinking tumbler	166	199	<LLD	<LLD	0.2
22	Vase, from automobile	215	807	0.14	8.2	5.8
23	Opaque-rimmed goblet	411	295	0.14	9.7	19.5
24	Footed candy dish, base	378	215	<LLD	1.8	1.3
25	Dessert dish (one of a set of two)	145	320	<LLD	0.5	4.0
26	Dessert dish (two of a set of two)	141	326	<LLD	0.1	0.7
27	Spoon holder	440	138	<LLD	<LLD	0.2
28	Short-stemmed wine glass	100	—	<LLD	<LLD	0.1
29	Dental amalgam mortar; opaque (one of a set of three)	106	1,473	<LLD	5.4	8.4
30	Dental amalgam mortar; opaque (two of a set of three)	106	1,476	<LLD	6.4	9.1
31	Dental amalgam mortar; opaque (three of a set of three)	107	1,479	<LLD	6.4	8.3
32	Salt dish	51	892	<LLD	3.5	3.2
33	Small ash tray, opaque	77	2,008	0.04	<LLD	0.4
<i>Fiesta tableware</i>						
34	Gravy boat	528	1,653	3.9	470	96,100
35	Plate	244	2,388	10.6	31,800	304,000

* <LLD = less than lower limit of detection (LLD), which is $0.03 \mu g L^{-1}$.

viously not uniform, so these counts can only be regarded as qualitative. The net counts per gram are reported in Table 1.

RESULTS AND DISCUSSION

The counts obtained by the NaI detector indicate that all but sample 28 had higher-than-background gamma activity levels. The observed gamma counts did not correlate with any of the uranium-leaching data. The fluorescence test would appear to be a good screening technique for uranium-bearing glass inasmuch as all the glass samples, except the nonfluorescing sample 28, produced above-background counts. As a point of comparison for the counting data in Table 1, a 1-g sample of uranyl nitrate [$\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] suspended in a liquid scintillation vial 13 cm above the crystal face (this is the mean distance from the midpoint of the objects being counted to the crystal face) produced about 40,000 counts (net) in 60 min. Radioassay of selected pieces of the glass and ceramic pieces on an intrinsic germanium detector and multichannel analyzer showed the gamma activity to arise largely from the ^{238}U daughter products ^{234}Th and ^{234}Pa .

The presently proposed U.S. drinking water regulation (DWR) for uranium is $20 \mu\text{g L}^{-1}$ (U.S. EPA 1991a). It is clear from Table 1 that none of the deionized-water leachates, and only one of the acetic-acid leachates from the glass samples, exceeded this value. The surface of that single sample (sample 1) was frosted, presumably by the manufacturer's use of hydrofluoric acid. Such a treatment would increase the surface area of the glass and perhaps otherwise increase the leachability of the contained uranium.

The 4% acetic acid solution (similar to household vinegar) has been used to test for leachable lead in glazed ceramics (Schellenberg 1990) and in crystalware (Food and Drug Administration 1991). It represents the leaching that might be seen with acidic foods such as vinegar, orange juice, and tomato sauce. Many fruit and vegetable products are quite acidic—examples include vinegar (pH 2.4–3.4), wines (pH 2.8–3.8), apples (pH 2.9–3.3), limes (pH 1.8–2.0), and tomatoes (pH 4.0–4.4) (Weast 1970). The pH's of the acetic acid and nitric acid solutions used here were 2.4 and 0.2, respectively.

The 1.0-M nitric acid represents a worst-case scenario with respect to leaching as few, if any, foods would approach this level of acidity. In the majority of the glass samples, the quantity of uranium leached with 1.0 M nitric acid was greater than that with 4% acetic acid. In those cases where it was less, we may be seeing the depletion, with respect to uranium content, of a rind (extending inward from the glass surface) accessible to the leaching solution. Here too, however, the amount of uranium seen in solution was low, with only the frosted vase (sample 1) approaching the DWR.

The leaching behavior of the two Fiesta ceramic

samples was in marked contrast to the limited leaching seen with the glass samples. Acetic acid leach solutions here had uranium concentrations that were about 24 to 1,600 times the DWR (Table 1). With all three test solutions, the uranium in the red Fiesta glaze was clearly more readily leached than that in the glasses. The red glaze used in this study was reported (Huxford and Huxford 1984) by the manufacturer to contain 14% uranium oxide (U_3O_8) by weight. We can compare the leaching results of this study regarding "Fiesta" items with work by Brown (1981) who investigated "Mexican Hat" items, manufactured by another company but also having an orange, uranium-bearing glaze. Brown's leachant solutions included Alka-Seltzer,[®] lemonade, lemon juice, and household white vinegar (5% acetic acid), with the latter solution yielding the highest uranium concentrations. A Mexican Hat jug and tumbler were studied and, with 24-h contact periods, the uranium concentrations in the vinegar were about 10,000 and 25,000 $\mu\text{g L}^{-1}$; this compares with the 470 and 31,800 $\mu\text{g L}^{-1}$ reported in Table 1 of this study for the two Fiesta items.

CONCLUSION

The ingestion hazard from uranium associated with the culinary use of vaseline glass appears to be minimal. In contrast, significant leaching of uranium was observed from the Fiesta ceramicware, particularly with acidic solutions. As with the widely publicized lead-containing ceramic glazes, contact with acidic foods should also be avoided in the case of ceramics with uranium-bearing glazes.

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REFERENCES

- Brown, L. D. Assessment of the hazard associated with the use of uranium as a glaze for domestic china. Regina, Saskatchewan, Canada: Saskatchewan Department of Labor; Radiation Safety Unit report RSU 29/OT/1281; 1981.
- DiSantis, D. J.; DiSantis, D. M. Wrong turns on radiology's road of progress. *RadioGraphics* 11:1121–1138; 1991.
- Ebert, W. L.; Bates, J. K. The reaction of synthetic nuclear waste glass in steam and hydrothermal solution. In: *Scientific basis for nuclear waste management XIII*, proceedings of the Materials Research Society symposium, Pittsburgh, PA: Materials Research Society; ISBN 1-55899-064-X and ISSN 0272-9172; Vol. 176; 1990: 339–346.
- Food and Drug Administration. FDA advice on leaded crystalware. FDA Talk Paper T91-12. 1991.

- Graziano, J. H.; Blum, C. Lead exposure from lead crystal. *Lancet* 337:141-142; 1991.
- Huxford, S.; Huxford, B. The collectors encyclopedia of Fiesta. 5th ed. Paducah, KY: Collector Books; 1984.
- Landa, E. R. Buried treasure to buried waste: The rise and fall of the radium industry. *Colorado School of Mines Quarterly* 82 (2); 1987.
- McCormick, L. More consumer radiation sources. *Health Phys. Soc. Newsletter* 20(2):5; 1992.
- Schellenberg, K. A. Dependence of leachable lead in glazed ceramics on previous treatment: Determination by an improved dithizone extraction method. *Virginia J. Sci.* 41:28-32; 1990.
- Schuyler, P. Moving to Richland—II. *The New Yorker* 67(5):62-107; 1991.
- Sirr, S. A. "Hot" plate. *RadioGraphics* 11:1068; 1991.
- U.S. Environmental Protection Agency. Radiological quality

- of the environment in the United States. Washington, DC: U.S. EPA; Report No. EPA 520/1-77-009; 1977.
- U.S. Environmental Protection Agency. National primary drinking water regulations; radionuclides; proposed rule. *Fed. Register* 56:33050-33127; 1991a.
- U.S. Environmental Protection Agency. Drinking water criteria document for uranium. U.S. EPA Criteria and Standards Division. Cited in: *Fed. Register* 56:33118; 1991b.
- von Philipsborn, H. Uranium in Central Europe—an imaginary field trip from Theuern. Introductory remarks to the 5th Radiometric Seminar Theuern. In: *Hot particles from the Chernobyl fallout, proceedings of the 5th Radiometric Seminar, Theuern, Germany*: ISBN 3-925690-10-7; 1988: 9-12.
- Weast, R. C., ed. *Handbook of Chemistry and Physics*. 51st ed. Cleveland, OH: Chemical Rubber Co.; 1970: D-105.

CONCLUSION

The ingestion hazard from uranium associated with the ordinary use of vase-like glass objects to be minimal. In contrast, significant leaching of uranium was observed from the Fiesta ceramicware, particularly with acidic solutions. As with the widely publicized lead-containing ceramic glazes, contact with acidic foods should also be avoided in the case of ceramic with uranium-bearing glazes.

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REFERENCES

- Brown, L. D. Assessment of the hazard associated with the use of uranium as a glaze for domestic china. *Regulatory Toxicology and Pharmacology* 1:11-15; 1981.
- Food and Drug Administration. *Guidance for Industry: Radiological Safety Unit Report RSTU 1807* (1981).
- DeGroot, D. J.; DeGroot, D. M. Wrong turns on technology's road to progress. *RadioGraphics* 11:11-15; 1991.
- Eber, W. L.; Baker, J. K. The reaction of glaze-like material with glass in steam and hydrothermal solution. In: *Sol-gel: A new process for material management*. NIH, proceedings of the Materials Research Society symposium, Pittsburgh, PA. Materials Research Society, ISBN 1-55899-084-X and ISSN 0272-9172. Vol. 176: 1990: 139-146.
- Food and Drug Administration. FDA advice on leaded crystalware. FDA Talk Paper T91-12. 1991.

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The leaching behavior of the two Fiesta ceramic