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VARIATIONS IN ISOTOPIC CONTENT OF NATURAL URANIUM

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ABSTRACT

Uranium ore concentrates from seventeen world sources have been compared to a standard to determine variations in isotopic content. A spread of about 0.06 per cent of the U^{235} content was indicated for the concentrates analyzed. It will be observed that domestic sources showed much wider variations than those from other parts of the world.

VARIATIONS IN ISOTOPIC CONTENT OF NATURAL URANIUM*

In 1959, the Paducah Plant Laboratory observed apparent differences in the isotopic content of UO_3 received from suppliers of natural, unaltered, uranium. After this discovery, a program was initiated to determine if uranium ores differ with source. To facilitate the program, ore concentrates were obtained from eight foreign and eight domestic sources. Foreign sources included four from Canada, two from Australia, one from South Africa and one from Portugal. Domestic sources included two from New Mexico and one each from the states of Colorado, South Dakota, Wyoming, Utah, Washington and Oregon. Two lots were obtained from all except the Portuguese source. In addition, Belgian Congo pitchblende was secured from the National Bureau of Standards. Also, two natural uranium samples were obtained from the Oak Ridge Gaseous Diffusion Plant. One was their hexafluoride working standard of natural isotopic composition which they received from the Harshaw Chemical Company in 1947 (1). The other was an unaltered urano-uranic oxide sample prepared by them in 1944 and designated as Primary Normal (P.N. U_3O_8).

The nineteen samples mentioned above were analyzed relative to the Paducah Plant unaltered UF_6 standard. This particular standard was received by the Oak Ridge Gaseous Diffusion Plant from the Harshaw Chemical Company on October 11, 1951, in cylinder MD-748. The cylinder was held at ORGDP until February 1954 and shipped to Paducah. An attempt has been made to determine from what source this material was derived, but records have been destroyed. The only concrete information available is that Harshaw started out processing Belgian Congo ore, later added Canadian, and still later processed some domestic ores. Most of their total output was derived from Canadian sources. Thus, although the source of the Paducah Plant unaltered UF_6 standard cannot be traced, the most likely source is Canada.

SAMPLE PREPARATION

A carbitol extraction procedure was employed in recovering uranium from the sixteen ore concentrates and Belgian Congo pitchblende. Various

* This document is based on work performed at the Paducah Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

precautionary measures were exercised to minimize the possibility of isotopic contamination. New glassware was used for processing each of the samples, and all solutions used in the extraction procedure were analyzed for uranium content. The following table lists uranium concentrations of the various extraction solutions. Results preclude isotopic contamination exceeding 0.001 per cent of the value (0.000007 wt. % U^{235}) if it can be assumed that any uranium contaminant present had a maximum U^{235} enrichment four times that of natural uranium, which should be a safe assumption.

<u>Solution</u>	<u>ppm Uranium</u>
Backwash Solution	≥ 0.5
Salting Solution	≥ 0.3
HNO ₃	< 0.003
Distilled H ₂ O	< 0.003
Carbitol	< 0.003

Recovered uranium was converted to U_3O_8 by igniting in new platinum dishes over a bunsen burner before being fluorinated to UF_6 using elemental fluorine and a high pressure-high temperature fluorination system (2). Three precautions were exercised to minimize the possibility of isotopic contamination during the fluorination procedure. The low pressure volume of the fluorination system was thoroughly cleaned before use for ore concentrate samples. Secondly, new fluorination tubes were used for the U_3O_8 to UF_6 conversion. Finally, the fluorine used for the conversion was analyzed and found to contain < 5 ppm uranium. This amount cannot contribute an error greater than 0.002 per cent of the value (0.000014 wt. % U^{235}) if a conservative maximum isotopic enrichment of four times natural uranium is assumed for any uranium contaminant.

A minimum of two extractions were performed on each lot of ore concentrate giving a total of at least four extractions on all but the Portugese and Belgian Congo sources. The second extraction on each lot was performed approximately four months following the first in order to include any long term analytical variables. At least four fluorinations were prepared from each extraction, giving a minimum of sixteen fluorinations for all but the Portugese source.

SPECTROMETER ANALYSIS

The analyses obtained were the ratios of mol ratios ($U^{235}/U^{234}+U^{238}$) of ore concentrates to the Paducah Plant unaltered UF_6 standard (3,4). Two CEC Model 21-220 gas analysis mass spectrometers were used in each measurement. Before initiating the analytical procedure, the spectrometers were equipped with clean ionization sources and inlet systems, after which they were conditioned with the Paducah Plant unaltered UF_6 standard. The inlet systems were of the two-position type equipped with a single leak to avoid leak fractionation effects.

In making the measurements, at least two containers of standard material were used in the analysis of each sample fluorination. Also, sample and standard were alternated between the two positions of the inlet system.

In general, four relative spectrometer determinations were made on each fluorination, two on each of two spectrometers. Thus, approximately sixteen determinations were performed on each extraction, 32 on each lot, and 64 on the ore concentrate from each world source. In the tables which follow, some deviations will be noted from these totals because of low UF_6 yield in a few fluorinated samples. Also, three extractions were made on a few lots.

DISCUSSION

It will be noted in the tables that domestic ore concentrates from Colorado, New Mexico and South Dakota were 0.04 to 0.05 per cent lower in U^{235} content than the Paducah Plant standard. The Utah and Wyoming concentrates analyzed were 0.02 to 0.03 per cent lower. Those from Oregon and Washington differed very slightly from the standard, with the Oregon source being the highest of the domestic ores analyzed.

Differences among the foreign sources analyzed were comparatively small, with the total spread in the order of 0.03 per cent. The lowest was approximately 0.02 per cent lower than the standard and had as its origin the Northwest Territory of Canada. The highest was the Belgian Congo pitchblende which was about 0.01 per cent higher than the Paducah Plant standard.

Results here appear to be in substantial agreement with those reported by others. Hamer and Robbins (5) reported deviations from a standard to be less than 0.05 per cent, and failed to show significant differences between the twelve ores which they analyzed; however, they did not analyze ores from the continental United States where the greatest deviations are evident. Our analysis included many of the sources sampled by them; and, as noted earlier, the foreign concentrates gave a spread of only about 0.03 per cent. L. A. Smith (1) and W. R. Shields (6) have reported an overall spread in the order of 0.10 per cent. Senftle et al. (7) reported the spread on twelve ore samples analyzed at Y-12 to be within the experimental error of results; however, confidence intervals were too large to detect a spread less than 0.10 per cent. It should be pointed out that the spread of 0.06 per cent indicated here was obtained on ore concentrates produced at the mines, and that multiple mineral types are possible from many of the sources. Specific mineral deposits, such as those analyzed by others, possibly would exhibit a wider spread.

PRECISION OF RESULTS

The 95 per cent symmetrical confidence interval of ± 0.00013 quoted on lots is an external precision based on agreement between replicate extractions. This precision is considered more realistic than somewhat smaller internal precisions based on agreement of individual spectrometer determinations for each lot. Thus, the precision of ± 0.00010 quoted on ore concentrates for each world source is considered reliable if it can be assumed that lots from each source do not differ. At this level of precision, it was not possible to show differences between lots from any source.

CONCLUSIONS

There are significant differences in the isotopic contents of unaltered uranium ore concentrates produced in the various parts of the world. Eight domestic sources of ore concentrate have been analyzed, and a spread of 0.06 per cent was indicated. Nine foreign sources showed a spread of about 0.03 per cent. The overall spread of the seventeen sources was 0.06 per cent.

Although the overall spread indicated here is 0.06 per cent, larger deviations are considered possible if specific mineral deposits were analyzed.

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TABLE I
DOMESTIC ORES

Sample	Source	Lot No.	Extractions	Flourinations	Determinations	Ratio to Standard	Average Ratio for Sample	Percent Difference
Climax	Grand Junction, Colorado	291	2	8	32	0.99956±0.00013	0.99952±0.00010	-0.05±0.01
		311	2	8	32	0.99948±0.00013		
Mines Development	Edgemont, South Dakota	108	2	10	32	0.99956±0.00013	0.99956±0.00010	-0.04±0.01
		156	2	8	31	0.99956±0.00013		
Kermac	Ambrosia Lake District, Grants, New Mexico	14	2	8	31	0.99952±0.00013	0.99956±0.00010	-0.04±0.01
		92	2	8	31	0.99960±0.00013		
Homestake	Ambrosia Lake District, Grants, New Mexico	56	2	8	30	0.99962±0.00013	0.99961±0.00010	-0.04±0.01
		80	2	8	32	0.99960±0.00013		
Lucky Mc	Fremont County, Wyoming	20	2	8	32	0.99972±0.00013	0.99968±0.00010	-0.03±0.01
		62	2	8	32	0.99963±0.00013		
Uranium Reduction	Moab, Utah	555	3	12	48	0.99984±0.00013	0.99977±0.00010	-0.02±0.01
		624	3	12	48	0.99970±0.00013		
Dawn Mining	Ford, Washington	55	3	12	48	0.99983±0.00013	0.99989±0.00010	-0.01±0.01
		72	3	12	48	0.99995±0.00013		
Lakeview	Lakeview, Oregon	2	2	8	32	1.00016±0.00013	1.00012±0.00010	+0.01±0.01
		16	2	8	32	1.00008±0.00013		

TABLE 2
FOREIGN ORES

Sample	Source	Lot No.	Extractions	Fluorinations	Determinations	Ratio to Standard	Average Ratio for Sample	Percent Difference
Rayrock	Marion River Area, Northwest Territory, Canada	R-26	2	10	32	0.99990±0.00013	0.99983±0.00010	-0.02±0.01
		R-41	2	8	32	0.99976±0.00013		
Faraday	Bancroft Area, Eastern Ontario, Canada	F-93	2	8	32	0.99983±0.00013	0.99986±0.00010	-0.01±0.01
		F-103	2	8	32	0.99988±0.00013		
Lorado	Lake Athabaska Area, Saskatchewan, Canada	111	3	12	47	1.00004±0.00013	0.99997±0.00010	0.00±0.01
		160	3	14	43	0.99990±0.00013		
Algom	Blind River Area, Ontario, Canada	753	2	8	32	1.00001±0.00013	1.00002±0.00010	0.00±0.01
		942	2	8	32	1.00002±0.00013		
Rum Jungle	Rum Jungle, Australia	120	2	8	32	0.99987±0.00013	0.99986±0.00010	-0.01±0.01
		124&125	2	8	32	0.99984±0.00013		
Radium Hill	Radium Hill, Australia	Z-62	2	8	32	0.99984±0.00013	0.99988±0.00010	-0.01±0.01
		Z-71	2	8	32	0.99993±0.00013		
Calprods	South Africa	53	2	8	32	0.99996±0.00013	0.99994±0.00010	-0.01±0.01
		142	2	8	32	0.99993±0.00013		
Portugese	Portugal	99	2	8	29	0.99985±0.00013	0.99985±0.00013	-0.01±0.01
Pitchblende	Belgian Congo	NBS	2	16	65	1.00014±0.00010	1.00014±0.00010	+0.01±0.01
ORGDP Hex. N.	ORGDP (1)		none	5 tubes	92	1.00010±0.00010	1.00010±0.00010	+0.01±0.01
P.N. U ₃ O ₈	ORGDP		none	24	96	1.00011±0.00010	1.00011±0.00010	+0.01±0.01