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A Procedure for the Determination of Uranium on Cellulose Air-Sampling Filters by Photon-Electron-Rejecting-Alpha-Liquid-Scintillation Spectrometry

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A PROCEDURE FOR THE DETERMINATION OF URANIUM ON CELLULOSE AIR-SAMPLING FILTERS BY PHOTON-ELECTRON-REJECTING-ALPHA-LIQUID-SCINTILLATION SPECTROMETRY

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A PROCEDURE FOR THE DETERMINATION OF URANIUM ON CELLULOSE AIR-SAMPLING FILTERS BY PHOTON-ELECTRON-REJECTING-ALPHA-LIQUID-SCINTILLATION SPECTROMETRY

W. J. McDowell
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ABSTRACT

A procedure is described for obtaining from cellulose air-sampling filters the total uranium content whether it be in the form of metal, oxide, tetrafluoride or most other salts of uranium. It is demonstrated that the uranium content can be accurately assayed by low-temperature ashing of the filter paper, dissolving the ash in a mixed nitrate-sulfate system, extracting the uranium selectively into a scintillator containing a high-molecular-weight amine sulfate, and counting the extract using a Photon-Electron-Rejecting-Alpha-Liquid-Scintillation (PERALS) spectrometer.

1. PROCEDURE

The filter paper (up to 2 in diam.) is folded and placed in a 16 mm × 60 mm (2 dram) screw-cap borosilicate glass vial. The uncapped vial is placed in a muffle furnace at 500°C. This temperature is just below the annealing temperature of borosilicate glass. Fifty such vials can easily be placed in a wire rack and into the furnace as a unit. After a period of about two hours, the filter paper is completely ashed leaving only a very minute amount of residual ash.

The vials are removed from the furnace, cooled until just warm to the touch, and the following reagents are placed in each vial: concentrated nitric acid 2 to 6 drops, sufficient to wet all of the ash; three drops of 30% hydrogen peroxide; and one drop of a saturated solution of aluminum sulfate. After these reagent additions, the vials are

placed in a heating device to, first, aid in dissolving the ash and, second, to drive off the nitric acid (B.P. 170°C). The latter is important since the presence of nitrate interferes with the extraction of uranium into the amine sulfate scintillator. A muffle furnace set at 200°C serves well for this purpose but prolonged exposure to nitric acid fumes may damage such a furnace; therefore, construction of an open-topped furnace or heater for this step with radiant heat from the bottom and sides (and possibly from infrared lamps over the top) is recommended. Commercially available devices may also be suitable.

When all the liquid has been evaporated from the vials and the residue is quite dry (after a period of 30 min to 1 hr), the vials are removed from the source of heat and allowed to cool slightly. Two mLs of a solution 1.0 M in sodium sulfate and 0.01 M in sulfuric acid is added to each vial. The vials are capped with a screw cap with a conical polyethylene insert, inverted several times each, and observed to be sure that all of the solid material is in solution. Slight warming of the vial to affect solution may be necessary in some cases.

After all of the solids are dissolved, a measured quantity of the extractive scintillator (1.2 to 2.0 mL) is added to the vial. The extractive scintillator is compounded as follows.

Dissolve 96 g of molecularly distilled "Adogen 364" (or other similar branched tertiary amine) in 600 mL of distilled-in-glass toluene and contact this solution with 100 mL of 0.9 to 1.0 N H_2SO_4 by shaking for 2 to 5 min in a separatory funnel. To the equilibrated and separated organic phase add 180 to 190 g of scintillation grade naphthalene and 4.0 grams of PBBO [2-(4'-biphenylyl-6-phenylbenzoazole]. Make this to a 1 L

volume and stir for several hours. Filter the solution through coarse filter paper to remove any undissolved PBBO and store in a brown bottle or bottle covered with aluminum foil. Although the scintillator is not really very light sensitive it does develop a light yellow color when exposed to room light continuously over a period of months.

Recap the vial with the polyethylene lined cap and equilibrate the two phases by repeated inversion for 2 to 3 minutes.

After the two phases have cleanly separated, pipette 1 mL of the organic phase into a 10 × 75 mm culture tube and sparge for 1 min with a dry, oxygen-free gas to remove dissolved oxygen. A disposable, 9-inch Pasteur pipette is used as a sparging lance. The sample is then corked and placed in a PERALS detector. These equilibration, sampling, sparging, and placing-in-detector steps are illustrated in Fig. 1 except that in the illustration a small separatory funnel is used as the equilibration vessel in place of a vial. Deoxygenation by sparging with an oxygen-free gas improves energy resolution and beta gamma rejection by pulse-shape discrimination but may not be necessary if the best energy and pulse shape resolution are not needed. A photograph of the PERALS detector is shown in Fig. 2, and a complete description is given in Ref. 1. Figure 3 shows a conceptual arrangement that would allow sparging/deoxygenation of several samples simultaneously. Figure 4 shows a typical spectrum of ^{234}U obtained in this procedure. In all the samples in this set from Y-12 air samplers, the alpha from ^{234}U was predominant. Some lower-energy contributions from ^{235}U and ^{236}U are also visible in a logarithmic display.

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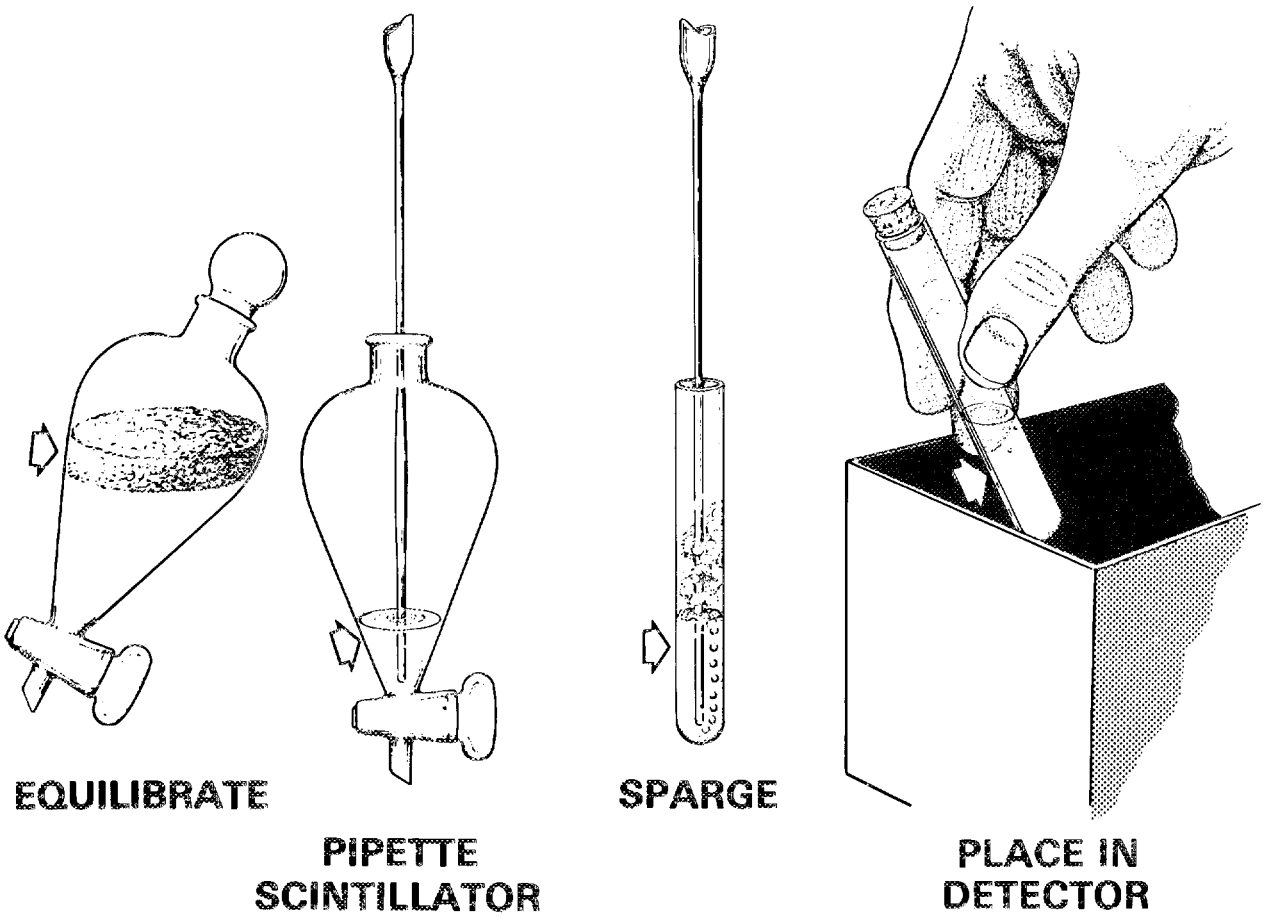

Fig. 1. The equilibration, sampling, and deoxygenation steps in the preparation of a sample for good energy resolution and beta-gamma pulse-shape rejection by the PERALS spectrometer.

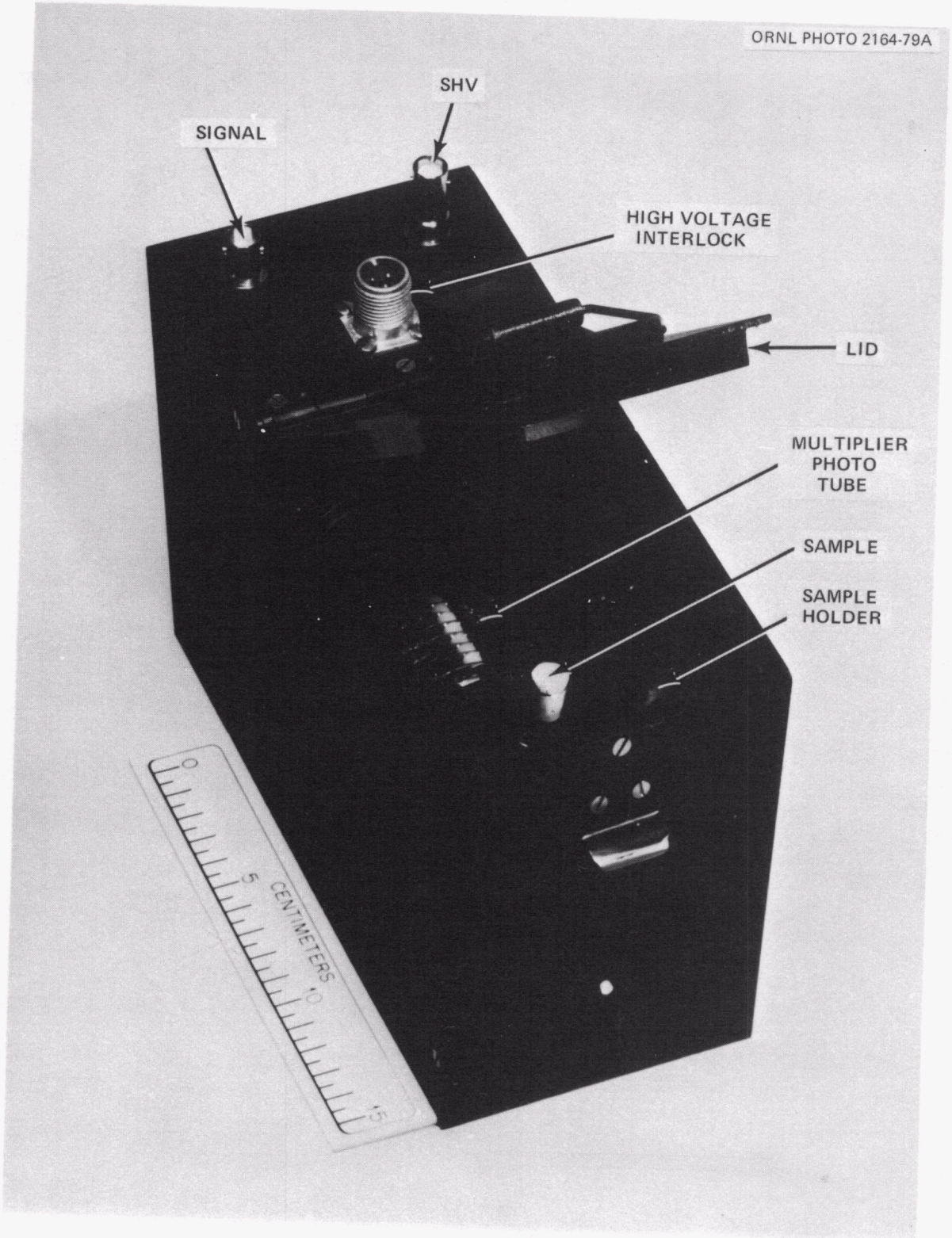

Fig. 2. A photograph of a PERALS detector with lid open showing the sample in place. The complete PERALS system requires a linear amplifier, a pulse, shape discriminator and a multichannel analyzer in addition.

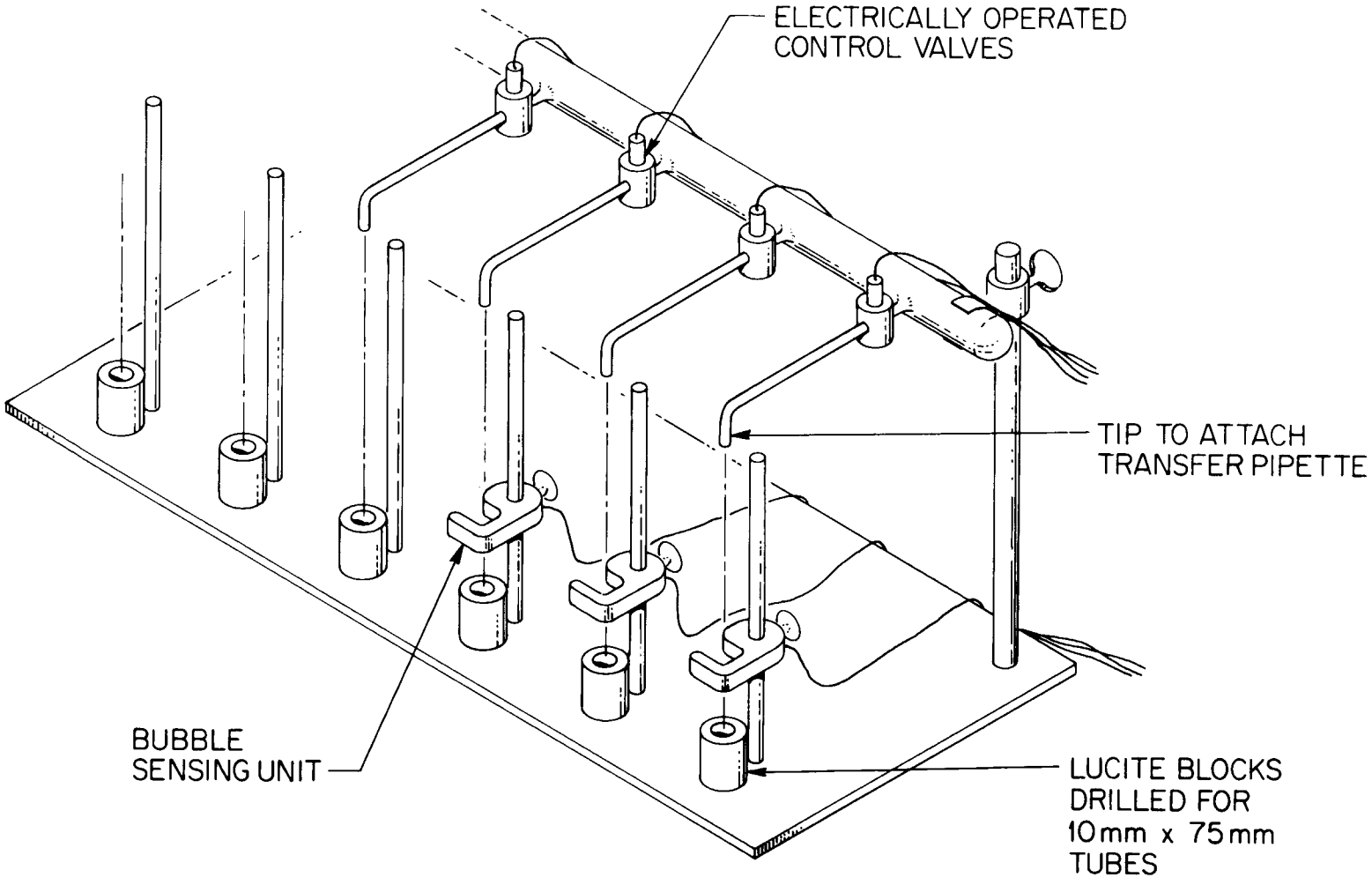

Fig. 3. An automatic sparging unit capable of deoxygenating several samples simultaneously.

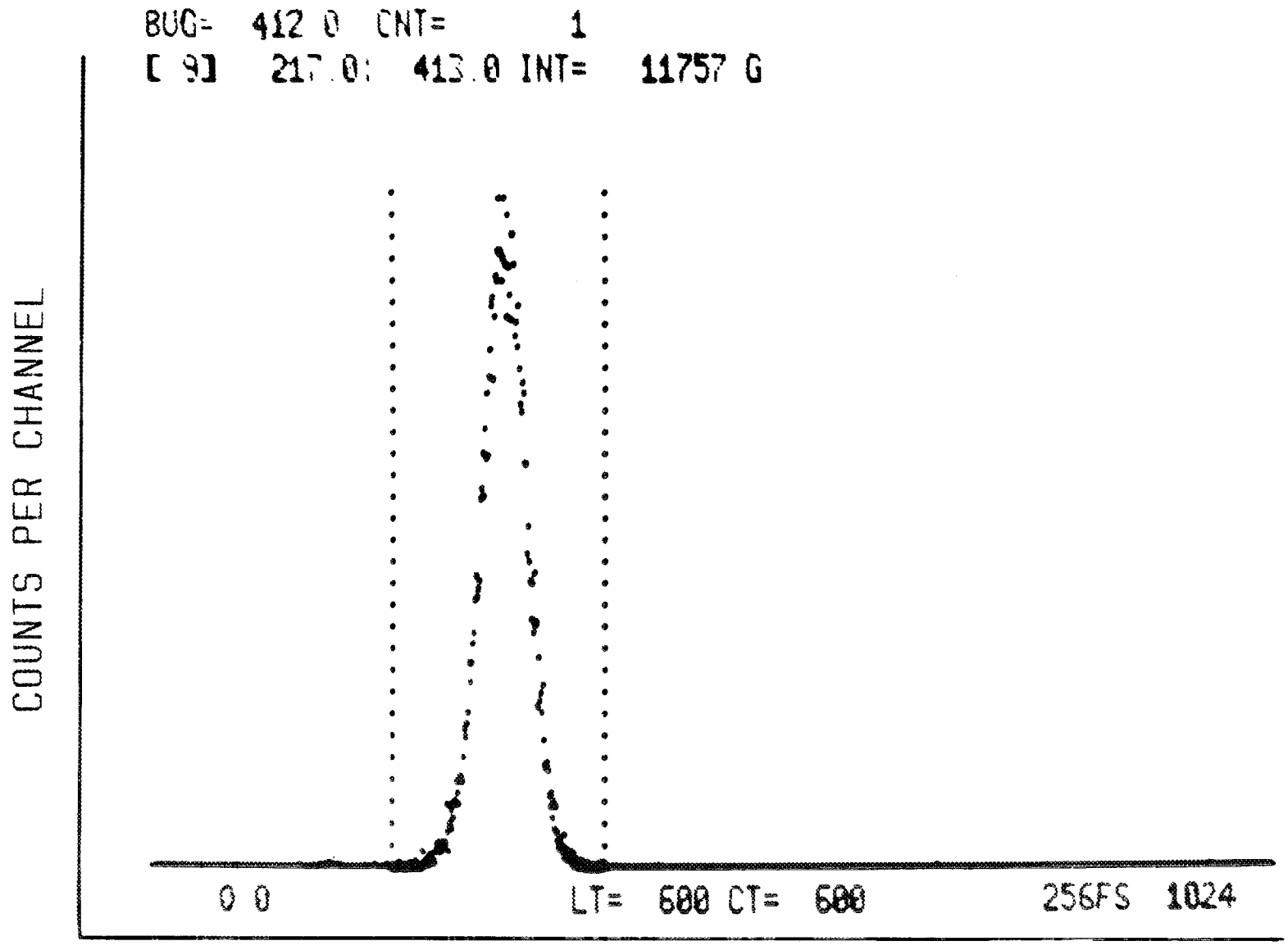

Fig. 4. A typical alpha spectrum obtained by PERALS from a Y-12 filter.

As in any radiometric determination, counting time to obtain counting statistics of the required accuracy appears to be the sample-throughput-limiting step; thus, it is expected that for large numbers of samples, multiple counters multiplexed into one or more multichannel analyzers will be necessary if more than about 20 samples of low activity are to be counted in a 24 hour period. Lower accuracy requirements and higher-count-rate samples would, of course, improve sample throughput capability.

2. RESULTS AND DISCUSSION

The accuracy of uranium determination by this method is limited both by the chemical manipulations and by the counting accuracy. The dissolution of standard U_3O_8 and UF_4 by the procedure was shown to be quantitative and reproducible within counting statistics. Counting accuracy is, of course, dependent on the total count collected with the standard deviation of the count, σ, being the square root of the count. Since the background in this counting method is very small (of the order of 0.03 cpm) the uncertainty of the background is not considered. With total counts of 10,000 the standard deviation is 1.0% of the recorded value. Counting is nearly 100% efficient. Alpha particles colliding with the wall of the sample vessel instead of interacting with the scintillator are ~0.32%, thus actual counting efficiency is 99.68% as determined by counting 6 aliquots of a NBS U_3O_8 standard.[1]

In this investigation an attempt was made to measure the reproducibility of the recovery of uranium from filter paper by pipetting 50 microliter samples of a stirred suspension of finely divided U_3O_8 onto

50 cm diameter filters, drying them, and carrying them through the procedure outlined. From a set of five samples, a standard deviation from the mean of 1.5 % was obtained. Since extraction coefficients for uranium from 1 M sulfate, 0.01 M sulfuric acid are between several hundred and one to two thousand, measurable losses of uranium in this step are not expected. Pipetting errors are probably the largest errors encountered in this procedure.

An independent comparison of material balances obtained in some two-phase uranium extraction experiments by fluorimetric-analysis and PERALS-analysis may be seen in Table 1. The fluorimetric analyses averaged over 20% lower than the liquid scintillation analyses, and the data were also more scattered.

Table 1. Comparison of material balances on two-phase liquid-liquid equilibrations by fluorimetric and PERALS analysis

Equil. No.	Fluorimetric			PERALS		
	Organic	Aqueous	Σ%	Organic	Aqueous	Σ%
1	0.978	0.106	89.5	0.818	0.923	95.7
2	0.822	0.121	86.9	0.714	0.102	95.2
3	0.628	0.124	81.6	0.587	0.118	97.2
4	0.458	0.127	81.7	0.420	0.114	94.4
5	0.329	0.141	73.3	0.364	0.126	97.2
6	0.205	0.151	61.2	0.282	0.153	96.5
7	0.157	0.145	69.0	0.159	0.182	95.4
8	0.098	0.174	63.0	0.119	0.209	96.7

Analyses of 28 rilters from air samplers supplied by Y-12 are shown in Table 2. The samples were prepared for counting on PERALS as outlined above in Section 1. PROCEDURE. They had previously been counted by the standard direct counting zinc sulfide method used at Y-12, and these values are included for comparison. The values obtained from PERALS spectrometry average 36% higher than those obtained by direct zinc sulfide counting indicating that, at least for these samples, the paper factor loss used in correcting the direct counting result is too low. In direct counting, alpha counts can be easily lost by deep embedding of the particulate in the filter paper or by the presence of large uranium or oxide or salt particulates from which alpha particles would not escape if the decay were in the interior of the particulate. Accurate correction of direct counting of filters to true uranium content would be impossible without a prior knowledge of particle size distribution and depth of particulate embedment in the filter. It is known that particles of alpha emitting material larger than 15 microns in diameter suffer from self absorption of alpha radiation.[2]

3. CONCLUSIONS

The procedure using PERALS spectrometry is recommended as a method of counting air samples filters for alpha activity. Radon daughters are not a problem since beta events in the decay chain are rejected by PERALS pulse-shape discrimination, and alpha events can be separated by energy differences (other significant alpha decay branches in the series have energies > 6.0 MeV). Sample preparation is relatively simple and may be preferred to that of the fluorescence technique now used as the standard

Table 2. Comparison of air-sample filters counted on plate and by PERALS

Sample No.	Date	DPM as counted on filter (ZnS)[a]	DPM PERALS[b]	Ratio PERALS / ZnS
12RF10	5/7/86	3044	5340	1.75
12PF13	5/5/86	1757	2716	1.55
12RF10	5/5/86	16625	23845	1.43
11NF22	5/6/86	1925	4982	2.59
11NF02	5/5/86	2208	1792	.81
11NF28	5/5/86	74091	83332	1.12
11NF22	5/5/86	5054	7258	1.44
11NF03	5/30/86	2213	2374	1.07
11NF35	4/30/86	3105	5031	1.62
11NF22	4/28/86	1788	5154	2.88
12RF10	4/24/86	2023	3767	1.86
11NF22	4/24/86	16731	36773	2.20
11NF22	4/22/86	5205	10649	2.06
12PF13	4/25/86	39615	40907	1.03
12PF12	4/25/86	4337	7026	1.62
12PF13	4/23/86	26816	33218	1.24
12PF12	4/23/86	5034	5877	1.17
11NF22	4/23/86	7847	28684	3.66
11NF35	4/23/86	1646	4179	2.54
11NF50	4/23/86	2191	1763	.80
12PF13	4/21/86	3125	3813	1.22
12PF13	4/16/86	12655	13757	1.09
12PF12	4/18/86	3298	3622	1.10
11NF22	4/21/86	10562	27229	2.58
12RF10	4/16/86	13086	18224	1.39
11NF22	4/17/86	3018	8470	2.81
11NF22	4/18/86	2136	4013	1.88
11NF35	4/16/86	6549	6946	1.06

[a]Counts converted to DPM using counter efficiency from standard

[b]Absolute counts

routine assay method. Although the additional sample preparation steps may be considered prohibitive as regards time and cost compared to direct counting of the filter papers, the use of the PERALS method should seriously be considered as the method against which direct counting is calibrated. The accuracy and reliability of this counting method is documented in reference 1.

4. ACKNOWLEDGMENTS

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