down to maintain the mixture at a brisk rate of boiling (setting of 60) and increase the flow of gas to approximately 40 ml. per minute. Distill for 1 hour, collecting the distillate in the absorber tubes. At the completion of the distillation, disconnect the aeration apparatus and transfer the contents of the absorber tubes to a 100-ml. volumetric flask. Wash each absorber with 10 ml. of water and 15 ml. of isopropyl alcohol. Make the volume to 100 ml. with isopropyl alcohol. Mix well and transfer a suitable aliquot to a 125-ml. boiling flask. Calculate the amounts of water, sodium peroxide solution, and isopropyl alcohol contained in the aliquot taken and add sufficient amounts of each to the flask to make 3.5 ml. of water, 5 ml. of sodium peroxide solution, and 11.5 ml. of isopropyl alcohol in the flask. The stipulated ratio of 11.5 ml. of isopropyl alcohol to 8.5 ml. of total water is critical. For a 10-ml. aliquot add 1.1 ml. of the 2% sodium peroxide solution and make up to 20 ml. with a mixture of 5 parts of Na_2O_2 solution, 3.5 parts of water, and 11.5 parts of isopropyl alcohol. Place two or three glass beads in the boiling flask and proceed as in the second paragraph in "Preparation of Standard Curve." Run a blank on the reagents and subtract it from the sample reading. Determine the chloropicrin content of the sample from the corrected absorbance and the standard curve.

Volatile substances which act as buffering agents are obtained from some agricultural products during the distillation. Add sufficient hydrochloric acid to neutralize these materials, to prevent interference with the normal color development in the determinative step. The formation of a yellow or orange color at this step usually indicates the presence of such materials.

Run a blank with each batch of samples.

Results and Discussion

Blank values from reagents and untreated food products are given in Table I, which shows that the reagent blank accounts for most, if not all of the food blanks found.

All recovery values are high (Table II) except for the broiler feed, where no great effort was expended to improve the recovery. Although this increases the uncertainty of residue found in the broiler feed, the values reported are consistent. Because of this lower recovery, the values reported for residue content are corrected for 65% recovery, but other residue values are not corrected (Table III).

The residues of chloropicrin found after fumigation and aeration are given in Table III, which shows that, other conditions being equal, the physical state of the material may be an important factor in the amount of initial residue. Flour, toasted corn flakes, and broiler feed in Series 1 all have about the same initial content, while corn, beans, and peas, all large particles, are very much lower. Table III shows that aeration removes most of the chloropicrin.

The fumigations reported here are much more rigorous than fumigations of warehouses in which these commodities might be stored. In these laboratory tests, there was no chance for the fumigant to escape. In Series 1, where the chemical was vaporized into the chamber at reduced pressure, all of the fumigant was present from the beginning of the 24-hour period. In most fumigations, more nearly simulated by Series 2, the fumigant is applied as a liquid on an absorbent pad and allowed to vaporize during fumigation. Under actual space fumigation conditions, the fumigant is likely to leak from the building, so residues would probably be still lower than those found in Series 2. In Series 1, an effort was made to produce conditions giving high residue, such as puncturing packages to allow free access of the fumigant. This is reflected by the fact that residues found are higher than in Series 2.

Biscuits were made from flour samples, to determine if the fumigant would persist in baked food, using the formula: 2 cups of flour, 3 teaspoons of baking powder, 1 teaspoon of salt, 6 tablespoons of shortening, and $^3/_4$ cup of milk. They were baked in a 450° F. oven for 15 minutes. In Series 1, where the initial residue values were high, a residue of chloropicrin remained in the biscuits (Table IV). Biscuits from Series 2 showed no residue.

Acknowledgment

The authors acknowledge the help of Dow personnel A. E. Doty and D. Anthony in fumigations and sample preparation, respectively, and G. E. Lynn, in planning the experiment. C. A. Snell of Foster D. Snell, Inc., New York, supervised the residue determinations which were carried out by Josef Blicharz.

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Received for review December 23, 1964. Accepted August 30, 1965.

FALLOUT DETERMINATION

Separation and Recovery of Fallout Cs^{137} from Zr-Nb^{95} in Forage Samples

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Forages provide a means of monitoring environmental fallout contamination and also provide data on one of the important steps in the passage of Cs^{137} through the dairy food chain of man. During periods of fresh fallout deposition this radionuclide cannot be determined directly by gamma-ray spectral analysis because of interference from gamma-rays of shorter lived nuclides, principally Zr-Nb^{95}. Since it is of importance to have rapid values of Cs^{137} contamination levels for predictive purposes, a chemical separation method applicable to environmental forage samples is necessary. This method was developed immediately after the 1961–1962 nuclear testing series and became of value again in the summer of 1965 to separate Cs^{137} from Zr-Nb^{95} caused by the spring Chinese nuclear test.

Experimental Methods

Forage samples were harvested from the University Farm near Fort Collins. Grass samples were cut from pasture and hay samples consisted of alfalfa

In forage samples contaminated with fallout soon after testing of nuclear devices, the biologically important Cs^{137} could not be calculated directly from a gamma-ray spectrum of the sample because of Compton interference of other gamma-ray–emitting radionuclides. The predominant interference was due to Zr-Nb^{95}, which was separated from the Cs^{137} activity by digestion of ashed forage samples in concentrated NaOH. The recovery of Cs^{137} by the method was 90% and the decontamination for Zr-Nb^{95} approximately 97%.

harvested in the spring of 1963. Grass samples were oven-dried at 90° C. and both grass and hay samples were ground through a hammer mill with a $^1/_8$-inch screen. Gamma-ray spectrometry was accomplished with a 4- × 8-inch NaI (Tl) scintillation crystal shielded from background by a 5-inch-thick steel-walled chamber and connected to a 400-channel pulse height analyzer.

The impossibility of direct gamma-ray spectrometric determination of Cs^{137} in forage samples exposed to fallout debris of recent origin was readily apparent. Compton interference, primarily from Zr-Nb^{95}, which exceeded Cs^{137} activity by one to several orders of magnitude, completely obscured the total absorption peak of Cs^{137}. The other interfering gamma-ray–emitting nuclides in fallout are $Ce^{141, 144}$, I^{131}, Sb^{125}, $Ru^{103, 106}$, and Mn^{54}, which are all of lower fission yield or have their principal gamma-ray energies sufficiently different from Cs^{137} to give less interference. In theory it is still possible to determine Cs^{137} under these conditions by either mathematical or analyzer spectrum stripping (*6*). In practice, however, with the relatively low levels of Cs^{137} compared to Zr-Nb^{95}, amplifier or phototube gain shifts of fractional channels produced very large discrepancies in the Cs^{137} estimate.

It was concluded that spectrum stripping would not provide the necessary precision and that the samples would have to be stored to allow for Zr-Nb^{95} decay (about one year) or the Cs^{137} separated by wet chemistry. Published procedures (*1*, *3*, *7*) for the chemical separation of Cs^{137} from mixed fission products produced desirable separation and recovery in our laboratory with completely soluble tracer solutions of Cs^{137}. However, it became apparent that the fallout Cs^{137} in forage samples was not completely soluble in the reagents used to leach or digest it. It appears that cesium has been assumed to be readily solubilized in environmental samples. Such is not the case, as found by gamma-ray spectrometry of the samples before and after treatment of dried forage samples by water extraction and by extraction and digestion with a variety of acids and acid combinations. Likewise, the Cs^{137} contained in forage ash was not completely soluble in a variety of acids and acid combinations. The acid treatments not only failed to solubilize Cs^{137} but also did not separate Cs^{137} from Zr-Nb^{95} and other interfering gamma-ray emitters.

A simple method based on digestion of the ash with concentrated NaOH produced complete solubility of Cs^{137} and sufficient separation from Zr-Nb^{95} for analysis by gamma-ray spectrometry of low activity samples.

Procedure. Dried forage (200 to 300 grams) was ashed at 360° C. in a stainless steel beaker. The ash was cooled, 50 ml. of a solution containing 100 grams of NaOH and 10 mg. of CsCl were added, and the mixture was digested for 3 hours on a hot plate. Distilled water was added as needed to maintain a constant volume. At the end of the digestion period, 500 ml. of hot water were added and solution was filtered through Whatman No. 52 filter paper on a Büchner funnel under vacuum. The residue was washed with 150 ml. of 10% NaOH. The filtrate was made up to 1 liter in a 1-liter polyethylene bottle and counted by gamma-ray spectrometry. The residue can be dried and counted. The size of sample will depend upon the activity of the forage and the precision desired. Large samples (200 and 300 grams) are needed because of the low specific activity of the forage if the product is to be determined by gamma-ray spectrometry.

Results and Discussion

Figure 1 shows the gamma-ray spectra of two forage samples, clearly revealing the separation of Cs^{137} from Zr-Nb^{95} activity. In the spectrum of the entire dried grass sample, the Zr-Nb^{95} peak completely obscures all but $Ru^{103, 106}$ activity. In the filtrate Cs^{137} as well as Mn^{54} is readily apparent and there is no evidence of Zr-Nb^{95}. The original hay sample was counted as 1.35 kg. of dry matter in a standardized $2^1/_2$-gallon container atop the 4- × 8-inch crystal, the filtrate in a 1-liter polyethylene bottle lying down on the crystal, and the residue spread evenly on a 3-inch-diameter BM2133 filter pad, also centered on the crystal. To determine absolute activities of any radionuclide, calibrated standards of each radionuclide present or suspected were counted in each geometry to determine counting efficiencies and the spectrum stripping equations. Since the counting efficiencies for each gamma-ray emitter are the same ratio for each counting geometry, the three spectra for each sample in Figure 1 can be qualitatively compared and for this reason the ordinate of each spectrum has been omitted. The peak ratios of Cs^{137} to Zr-Nb^{95} in the three spectra illustrate the separation afforded by the method. The decontamination factor for Zr-Nb^{95} was greater than 40—that is, more than 97% was removed.

A series of separations on a hay sample of relatively high Cs^{137} specific activity but whose Zr-Nb^{95} activity had been lost by radioactive decay was used to determine the recovery. The Cs^{137} activity in this sample could be calculated directly from the gamma-ray spectrum by the spectrum stripping procedure. Subsamples of this hay were ashed and digested with NaOH as described in the procedure and the results are listed in Table I. The recovery was 99.2%, with a standard deviation of 4.7%. A series of samples using no cesium carrier showed 90 ± 5% recovery. The minimum detectable activity of Cs^{137} in a 1-liter filtrate fraction counted by gamma-ray spectrometry was 50 pc. Therefore, the minimum detectable concentration of Cs^{137} in forage samples, assuming a 250-gram aliquot was used, was 200 pc. per kg.

Table I. Recovery of Cs^{137} from Hay by NaOH Extraction

No.	Subsample[a] Weight, Grams	Cs^{137}, Pc./Kg.
1	100	3488
2	100	3367
3	100	3352
4	200	3651
5	200	3782
6	200	3570
7	300	3252
8	300	3353
9	300	3350
10	300	3492

Mean and standard deviation, 3466 ± 163

Mean recovery, 99.2 ± 4.7%

[a] Original sample 3494 ± 141 pc./kg. determined by ten counts of dry hay.

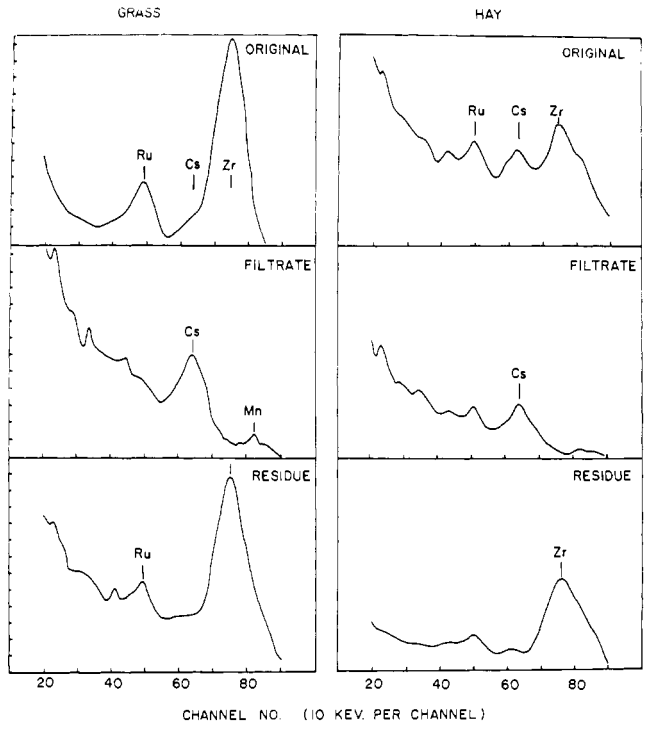

Figure 1. Gamma-ray spectra of original forage samples, filtrate, and residue fractions of NaOH separation method

Separation of Cs^{137} from $Zr\text{-}Nb^{95}$ by concentrated NaOH

Of the Cs^{137} activity present in a forage sample, part will be due to foliar absorption and contained in the plant tissues and part will be on the surface and unavailable because of insolubility. Plant uptake from soils in high-clay mineral soils has been shown to be negligible (*4*). The ratio of absorbed to surface-bound Cs^{137} in plants is important, as it determines also the amount absorbed from the gut of forage-fed animals and consequently that available for passage through the food chain of man.

The chemical state of fallout Cs^{137} is known only incompletely. The Cs^{137} in the primary fallout particle, in general, is probably soluble. The unavailable fraction found in plant samples seems to arise from wind-blown clay particles which bind the Cs^{137} on the plant surface. Clays of the platy type, such as montmorillonite, bind Cs^{137} very tenaciously and the complete removal of Cs^{137} from these soils usually requires a Na_2CO_3 fusion technique (*2*).

A comparison between the solubility of Cs^{137} in hay and grains provides evidence for a difference between Cs^{137} deposited on the surface and that contained in the plant. The Cs^{137} in grains must have arrived there by active transport within the plant, while the distribution between surface and cellular activity in forages is unknown. Further evidence for a fraction of Cs^{137} on the surface of plants was obtained by exposing growing plants to a sprinkler for 2 hours, which removed about 25% of the activity. Experiments in our laboratory revealed that about 45% of the Cs^{137} in alfalfa forage is water-soluble. On the other hand, grain samples in which the total Cs^{137} activity must be only that transported within the plant during exposure showed 70% of the Cs^{137} activity to be soluble in water.

Irreversible sorption by soil silicates is probably the reason why other separation techniques that are successful for tracer or ionic solutions are not suitable for environmentally contaminated samples. A large fraction of the total Cs^{137} forage activity is contained in clay mineral particles attached to the plant surface. Many silicate structures are known to be attacked and at least partially dissolved in high concentrations of hydroxyl ions (*5*) and Cs^{137} is evidently removed from the clay matrices by the NaOH method described here. Cs^+ is very soluble in strong base, while the fission product contaminant, $Zr\text{-}Nb^{95}$, is insoluble.

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Received for review March 19, 1965. Accepted August 23, 1965. Work supported by contract At(11-1)-1171 with the U. S. Atomic Energy Commission. Published with the approval of the Director of the Colorado Agricultural Experiment Station as Scientific Series Paper No. 1013.