

A NEUTRON ACTIVATION SCHEME FOR THE DETECTION AND DETERMINATION OF POLLUTANT HEAVY METALS IN SEWAGE BASED FERTILIZERS

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A scheme of analysis of heavy metals in sewage based fertilizers, based mainly on direct gamma spectrometry using a Ge(Li) detector, is described. Reversed-phase anion exchange chromatography was used in separating some of the elements with mutually interfering gamma energies. The results are compared with those obtained from atomic absorption and spectrophotometric procedures.

Introduction

One of the many useful aspects of environmental pollution control, is the agricultural utilization of fertilizers produced as a result of treatment of town wastes and effluents. The treated sewage sludges can be used on agricultural land either as composted sludge, or sprayed in liquid form. Both forms are produced by the action of aerobic bacteria, on the untreated sludge in oxygenated chambers. These fertilizers are extremely cheap, very rich in humus producing organic matter, trace elements, nitrogen, phosphorous, and potassium.¹

However, it has been recognised for some considerable time, that industrial effluents from industrial plants contribute to the composition of sewage sludges and agricultural fertilizers prepared from them. Spectrophotometry,²⁻⁴ atomic absorption,^{5,6} X-ray fluorescence,⁷ pulse polarography,⁸ fluorimetry,⁹ and flameless atomic absorption spectrophotometry¹⁰ have been used to determine metal pollutants in a variety of sludges, waters, effluents, soils and sediments.

During the last decade, neutron activation analysis, employing high resolution Ge(Li) detectors, has been used to determine trace metal concentrations in catalysts, sludge deposits, glass and steels,¹¹ iron ores,¹² human tissue,¹³ rocks,¹⁴ and geological samples.¹⁵ Neutron activation schemes incorporating radiochemical separations

have been used in the analysis of chromium,¹⁶ lunar samples,¹⁷ rocks,¹⁸ soil profiles,¹⁹ ocean water,²⁰ finger nails and hair.²¹

Although the main trend in the development of neutron activation analysis is towards high resolution gamma spectrometry, used in conjunction with suitable automated computer programmes,²²⁻²⁴ radiochemical separations are still necessary where the analytical problems cannot be solved by the direct approach, and the necessity to wait for long decay periods to determine an element is unpractical.^{25,26}

The method described in this paper, concentrates mainly on the use of purely instrumental activation analysis, using a Ge(Li) detector, and a multi-channel analyzer. A computer programme in FORTRAN was used to draw the gamma spectra from punched tape obtained directly from the multi-channel analyzer. Varying activation periods, and different decay times of the radio-nuclides were utilized during the determinations.

Reversed-phase extraction chromatography using liquid anion exchangers impregnated on paper, based on the work of BRINKMAN and de VRIES,²⁷ was used in separating mercury from selenium, and copper from other positron emitters. The determinations were carried out mainly on undried samples, as it was observed that, drying even at 60 °C led to volatility losses in some elements. Chromium, manganese, cobalt, nickel, zinc, arsenic, cadmium, antimony, and barium were determined by direct gamma spectrometry, selenium and mercury by radiochemical separation as well as direct gamma spectrometry, and copper by radiochemical separation followed by gamma spectrometry.

Photopeak areas were calculated using the "total peak area" (TPA) method, and the energy of the photopeak determined by comparison with an energy calibration graph obtained from gamma energy standards of appropriate magnitude. BAEDECKER,²⁸ in an excellent review on digital methods of photopeak integration in activation analysis, has studied the precision attainable by TPA, and methods proposed by COVELL,²⁹ STERLINSKI,³⁰ and QUITTNER,³¹ and considers a modification by WASSON of the TPA, the most advantageous, the TPA method being included as a second option in the computer programme used.

Experimental

Instrumentation

The high resolution gamma spectrometer was composed of the following components:

The Ge(Li) detector: A Canberra Model 7226, mounted in a cryostat assembly kept at near liquid nitrogen temperature. Right circular cylinder with 42 mm \varnothing drifted coaxially with one open end. Length: 18 mm, weight: 125 g, active area

facing window: 5 mm, energy resolution at 1.33 MeV: FWHM 1.97 keV, peak to Compton ratio: 20 : 1 for ^{60}Co , capacitance: 30 pF, efficiency for ^{60}Co : 3.4%.

Multi-channel analyzer: A series 1100 Analyzer System – a compact AEC modular, multi-channel analyzer consisting of the following modules: an Analog to Digital Converter Module which provides conversion gain selections of up to 1024 channels, the Data Handling Module, and the Memory Module.

Sample preparation

The fertilizer sample used throughout this work, was obtained from the Rye Meads Sewerage Disposal Works, Hoddesdon, Essex. Undried, air stabilized samples were used in most irradiations.

The bulk sample of about 1 kg was reduced to 100 g by quartering. Pieces of stone and pebbles were removed by screening. During the sealing of the preweighed irradiation samples into self-sealing polyethylene vials, two grammes of the sample was weighed out separately and used for moisture determination at 105 °C. The undried sample results were corrected for this moisture content.

Preparation of standards

For copper, nickel, cobalt, zinc, mercury, manganese and selenium, the specpure element was dissolved in A. R. grade nitric acid. For chromium, A. R. grade ammonium chromate dried under vacuum was used. For cadmium, A. R. grade cadmium acetate was used. For antimony, the specpure metal was dissolved in nitric acid and the antimony oxides converted to tartrate by treatment with tartaric acid. An arsenious acid solution was used for arsenic. The barium standard was prepared by dissolving A. R. barium carbonate in nitric acid. The compositions of the chromium, cadmium, and antimony standards were checked by atomic absorption and corrections made. Suitable aliquots of the standards were micro-pipetted to 1.2 cm \varnothing filter papers and air dried before being sealed in polyethylene containers.

Irradiation of samples and standards

The samples and standards were irradiated together in an aluminium irradiation canister, in a thermal neutron flux of $7 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, at AERE, Harwell. Irradiation times varied from 12 to 24 hrs.

Activity measurements

The sample and standards were counted using the Ge(Li) detector, with a uniform geometry, on non-irradiated vials. Before and after each counting session the multi-channel analyzer was calibrated using the appropriate gamma-ray standards.

Table 1
 The results obtained

No.	Element	Radio nuclides measured	Half-life	α -Energies used, MeV (abundances, %)	Experimental results, ppm	Mean value, ppm	Coefficient of variation, %
1	Cr	^{51}Cr	27.8 d	0.323 (10)	630, 740, 650, 620, 710, 720, 680, 690	680	6.4
2	Mn	^{56}Mn	2.586 h	0.847 (98.6)	690, 660, 570, 650, 540, 540, 545, 535	591	10.8
3	Co	^{60}Co	5.26 y	1.172; 1.333 (100)	22, 25, 19, 26, 26, 25, 19, 20	22.6	12.9
4	Ni	^{65}Ni	2.553 h	1.49 (18)	260, 250, 290, 190, 200	238	18.8
5	Cu	^{64}Cu	12.88 h	0.511 β^+	880, 850, 860, 960, 940, 930	903	5.1
6	As	^{76}As	26.8 h	0.559 (38)	14, 14, 18, 16, 18, 16, 16, 14	15.8	10.6
7	Se	^{75}Se	127 d	0.280 (23)	55, 58, 42, 49, 45, 40, 43, 44	47	13.9
				0.401 (12.5)			
8	Cd	^{115}Cd	2.2 d	0.335 (52)	85, 87, 98, 90, 87, 81, 80, 104	89	9.3
9	Sb	^{122}Sb	2.74 h	0.565 (66)	16, 17, 18, 19, 15, 15, 16, 15	16.4	9.2
		^{124}Sb	60.2 d	0.603 (98)			
10	Ba	^{131}Ba (^{131}Cs)	11.52 d	0.496	150, 150, 199, 180, 230, 220	188	19.0
11	Hg	^{197}Hg	2.7 d	0.077 (100)	42, 46, 49, 48, 47, 37, 34, 29	41.5	17.8
		^{203}Hg	46 d	0.279 (83)			
12	Zn	^{65}Zn	245 d	1.115 (50)	0.32%, 0.32%, 0.33%, 0.32%, 0.29%, 0.27%, 0.30%	0.31%	6.9

Isotopic data were obtained from the publication of ALIEV et al.³² and from the Isotope Catalogue for Instrumental Activation Analysis I, II, and III, by PAGDEN et al.³³

Radiochemical separations

Reversed-phase anion exchange chromatography using 0.1M solutions of Amberlite LA-1 and LA-2 in chloroform to impregnate Whatman's No. 1 chromatography paper was utilized. Various concentrations of hydrochloric acid was used as the eluant. The method proved satisfactory for the separation of any of the fifteen elements, Mn, Fe, Co, Cu, Zn, Se, Cd, Sn, Sb, Ba, Hg, Pb, Cr, As, and Ni from each other using a hydrochloric acid eluant from 0.5M to 9M as required.

Mercury from selenium and copper from other positron emitters were separated by a modification of the above procedure. The gamma energies of ²⁰³Hg, (0.279 MeV) and ⁷⁵Se, (0.280 MeV) are mutually interfering. The 0.511 MeV positron annihilation peak due to ⁶⁴Cu had to be separated from other positron emitters - in this case mainly ⁶⁵Zn.

The irradiated sample was dissolved under reflux with a small amount of nitric acid together with added mercury, selenium and copper carriers. Perchloric acid was added and reflux continued for a further 10 min. A suitable aliquot was applied as a 10" streak across an LA-2 impregnated paper. 9M hydrochloric acid eluant was used for the separation of mercury from selenium. The paper was air dried and located with 40% stannous chloride.

A separate LA-1 impregnated paper was used for the separation of copper. The eluant was 6M hydrochloric acid, and the locating agent, dithizone in benzene.

Mercury and selenium were also determined using the 0.077 MeV peak of ¹⁹⁷Hg, and the 0.401 MeV peak of ⁷⁵Se, by direct gamma spectrometry.

Table 1 illustrates the results obtained. Table 2 compares the NAA results, with those obtained from atomic absorption and visible spectrophotometric methods.

Discussion and conclusions

The greatest advantage of direct gamma-ray spectrometry is that, in one single simultaneous step it can reveal the presence of most trace elements present in a sample, whether the presence of the particular element is expected or not, and without resorting to specific tests for any element. Most of these elements can be determined quantitatively with varying degrees of precision, the limitations being partly due to the resolving power of the detection system, but mainly because of interference from the Compton backgrounds of isotopes with strong activity which

Table 2
Comparison of the NAA and other results

No.	Element	Method used	Mean of three results, ppm	Mean concentration using NAA, ppm	Difference, %
1.	Cr	Spectrophotometry	633	680	7.42
2.	Mn	Spectrophotometry	616	591	4.23
3.	Co	AAS	22.5	22.6	0.44
4.	Ni	AAS	269	238	13.03
5.	Cu	AAS	970	903	7.42
6.	As	Spectrophotometry	9.3	15.8	69.89
7.	Se	—	—	47	—
8.	Cd	AAS	126	89	41.57
9.	Sb	AAS	22	16.4	34.14
10.	Ba	AAS	250	188	32.98
11.	Hg	—	—	41.5	—
12.	Fe	Spectrophotometry	1.52%	—	—
13.	Pb	AAS	555	—	—
14.	Bi	AAS	138	—	—
15.	Zn	AAS	0.31%	0.31%	0.00

The spectrophotometric procedures used for chromium, manganese, arsenic and iron were the sym-diphenyl carbazide, ammonium periodate-permanganate, silver di-ethyl-dithio carbamate and the thioglycolic acid procedures respectively.

tend to impair the measurement of those isotopes with lower gamma energies, short half-lives, and weak activities. The intense activities of ^{24}Na and ^{42}K , if present in sufficient amounts can obliterate many of the shorter lived radionuclides. In the fertilizer samples used the activity due to ^{24}Na was not significantly high, although there was considerable activity due to ^{42}K . However interference with the 0.847 MeV ^{56}Mn peak, which was counted after an 8 hr decay period was minimal. The precision of nickel determined by measuring the 1.49 MeV peak would have been affected by that of ^{42}K (1.53 MeV), as potassium was obviously present in considerable amounts in the fertilizer. There was some degree of mutual interference between ^{76}As (0.559 MeV) and ^{122}Sb (0.565 MeV).

The precision can certainly be improved in some instances, if a radiochemical separation technique is employed. The determination of copper using a radiochemical separation technique shows the best precision. On the other hand a purely instrumental approach requires less time and can give an indication of the upper limits of a great number of trace elements present in the fertilizer.

For lead and bismuth atomic absorption is the best procedure as these elements cannot be determined by gamma spectrometry, and beta counting after radiochemical separation will not have any special advantage.

Iron has a high detection limit with neutron activation, and is best determined by other procedures.

Gamma spectra illustrating the relative elemental concentrations in sewage based fertilizers, or effluents from a given environment, can be related to the activities of industrial plants operating within that environment. In any future environmental pollution control scheme, a statistical survey, over a period of time, of relative elemental levels, can indicate any fundamental changes in the nature of effluents discharged in the environment.

A discussion of the toxic levels of elements detected in the Rye Meads fertilizer is beyond the scope of this work. This will primarily depend, not only on the actual metal concentration itself, but on the degree and selectivity of plant uptake of these elements. In addition, there is always the possibility that seemingly insignificant amounts of toxic heavy metals can be concentrated by plants. Some of these metals are known to accumulate irreversibly in the bodies of animals and man. Some form of continuous monitoring of the production of these fertilizers seems essential.

This scheme could utilize neutron activation in conjunction with other more economical methods such as atomic absorption and X-ray fluorescence. The latter two can be used for routine analysis of expected elements, whilst neutron activation analysis can be carried out at greater intervals, as a general survey, and also for the determination of very low levels of some accumulative toxic elements.

However, as LAITINEN,³⁴ in his series of editorials on the application of analytical chemistry to environmental pollution, has stated, to determine the true significance of pollutants on living things, the methods used, must be able to distinguish between various structural forms of these pollutants. Thus chromium(VI), is much more toxic than chromium(III); the methylmercuric ion is more dangerous than inorganic forms of mercury, as it is manufactured by micro-organisms and persists throughout the life chain, through fish and fish-eating animals.

The presence of mercury in untreated sludges can initiate a similar cycle through micro-organisms, plants, animals, and man. Therefore where structure is of paramount importance, the neutron activation scheme should be supplemented by analytical procedures able to determine the specific structure of the compounds involved.

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