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HEAVY WATER ORGANIC COOLED REACTOR

GAMMA-GAMMA COINCIDENCE COUNTING APPLIED TO CHLORINE ANALYSIS BY NEUTRON ACTIVATION

By

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FOR
GAMMA-GAMMA COINCIDENCE COUNTING APPLIED
TO CHLORINE ANALYSIS BY
NEUTRON ACTIVATION
AI-CE-35

Page 5

Last sentence should read:

The method has significantly extended the experimental sensitivity for chlorine detection to about 10 ppb on a 10-g sample, and at the same time has improved the precision and accuracy of the determination.

Page 9

Last sentence should read:

A sufficient amount of terphenyl was added to fill completely a 10-ml polyethylene bottle (~10 g).

Page 23

Second sentence should read:

For each analysis there is given $s(\hat{y})$, $\bar{y}$, percent relative $s(\hat{y})$, N , $\bar{x}$, and percent relative $s(\hat{y}_j)$ for an unknown whose x_j value is equal to the $\bar{x}$ value.

Page 28

Second paragraph should read:

By the new method one can determine chlorine in the 0.4- to 2-ppm range with a standard deviation of about 7% and down to about 10 ppb with a standard deviation of about 50%, using a 10-g sample. These precision and accuracy levels seem to be significantly better than those previously obtainable, and the experimental sensitivity for chlorine detection has been extended to a level that is much below the chlorine-impurity concentration range presently found in organic reactor coolants. Large samples must be irradiated in order to give sufficient chlorine activity to be observed by coincidence counting; however, this permits a more representative estimate of the chlorine content of the batch sampled.

Third paragraph should be deleted.

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ABSTRACT

Gamma-gamma coincidence techniques for radionuclide determination have been shown to facilitate activation analysis. A routine neutron-activation method for determining trace quantities of chlorine in organic coolants has been developed which eliminates the effect of interfering impurity activities. The method has significantly extended the experimental sensitivity for chlorine detection to about 10 ppb and at the same time has improved the precision and accuracy of the determination.

I. INTRODUCTION

Organic reactor coolants contain a chlorine impurity which may cause or contribute to problems of film formation, hydriding of zirconium, etc.⁽¹⁾ Analysis for the chlorine impurity associated with organic reactor coolants thus has received considerable attention. Shepard and Keen⁽²⁾ have summarized the methods which have been used to analyze for chlorine in organics. Of the methods, chemical determination, x-ray fluorescence, and neutron activation, the latter has proven most successful in the low parts per million ranges typical of most terphenyls.

The most frequently used procedure for chlorine activation analysis involves simultaneous thermal-neutron irradiation of the samples to be analyzed and samples of known chlorine content. The activating reaction is $\text{Cl}^{37} (n, \gamma) \text{Cl}^{38}$. The 37-min Cl^{38} product decays by beta emission followed by 1.64- and 2.16-Mev cascade gammas. One or the other of these gammas is detected in both standards and unknowns to yield the chlorine content of the unknowns by a simple comparison of the activities in the standards and unknowns.

Experience has shown, however, that the activation-analysis method is unreliable for organics when the chlorine content is low and certain other impurities are present whose induced activities interfere with the chlorine measurement. The major interfering activities are Mn^{56} , Na^{24} , and Ar^{41} ,⁽²⁻⁶⁾ all of which emit gammas close in energy to those emitted by Cl^{38} . Unfortunately, the reactor-grade organics always contain impurities which yield these activities upon irradiation.

Another problem associated with this analysis method has been noted by Edwards,⁽²⁾ who claims that thermal heating of a sample during reactor irradiation aids the diffusion out of the sample of produced hydrogen chloride gas, thereby giving a biased chlorine analysis.

The major goal of this investigation was to develop a method for determination of chlorine in organic materials, especially terphenyls, which would be accurate, precise, and not limited by these interfering activities. Although the activation-analysis method which has been extensively used gives better results than do other methods, it is now especially inadequate for terphenyls because

(1) improvements in reactor-grade quality have reduced their chlorine level to only a few ppm, and (2) use in a nuclear reactor causes additional chlorine loss, plus contamination by corrosion products.

Coincidence counting is possible with many radionuclides, but it has not been commonly used in activation analysis for detecting the desired activity, perhaps because of its low inherent efficiency. Owing to the "inert" matrix of terphenyl samples and since cascade gammas are emitted by Cl^{38} , it was anticipated that activation of large amounts of terphenyls would give sufficient Cl^{38} activity for determination by coincidence counting. The specificity of coincidence counting should permit achieving the desired goals.

II. EXPERIMENTAL

A. MATERIALS

Chlorine standard solutions were prepared from reagent-grade calcium chloride and sodium chloride which were dried at least 24 hr in an oven at 110°C and cooled in a desiccator over Drierite before weighing. A weighed amount of these salts was added to a 1-ℓ volumetric flask and dissolved with deionized-distilled water to give 1000-ppm chloride-ion stock solutions. The deionized-distilled water was obtained by passing distilled water through a Deem-A-Jet mixed resin. One- to 10-ml aliquots of these stock solutions were taken and diluted to 1 ℓ so as to give a series of chloride-ion standard solutions ranging from 1 to 10 ppm. Further 1-ℓ dilutions of these standards were made to extend the standard series down to a chloride-ion concentration of 0.25 ppm. A "blank" solution of deionized-distilled water was retained by carrying through the above-described dilutions but with no added salts. The standard solutions were stored in 500-ml polyethylene bottles. All containers were carefully cleaned in an identical manner with detergent, acetone, and deionized-distilled water. Special care was taken to avoid contaminating samples with chlorine from fingerprints or perspiration.

The organics analyzed in this study were reactor-grade terphenyls either as received from the manufacturer or after being used in an operating nuclear reactor.

For neutron irradiations, accurately measured 5-ml volumes of standard solutions were pipetted into 10-ml polyethylene bottles of thick-walled construction. These bottles are right circular cylinders 2-1/8 in. high, 11/16 in. inside diameter, and 13/16 in. outside diameter. The physical form of the terphenyls varied, being either powder, flakes, large chunks, or liquid. The powders and flakes were sometimes packed into one of the polyethylene bottles for irradiation, but at other times they were melted on a hot plate, as were the large chunks, and poured into a polyethylene bottle. A sufficient amount of terphenyl was added to fill completely a 10-ml polyethylene bottle.

B. IRRADIATION

All activations were performed in Irradiation Thimble No. 1 of the Shield Test and Irradiation Reactor (STIR). A description of this reactor is given in Reference 7. The maximum thermal- and fast-neutron fluxes for Thimble No. 1 are 1.25×10^{13} and 3.3×10^{12} n/cm²-sec, respectively.

The sample irradiation containment device consisted of a vertically stacked assembly of polyethylene buckets 2-1/8 in. diameter and 2-3/16 in. high. As many as three sample bottles could be placed in one bucket. Although the neutron flux in the irradiation thimble decreases with distance from the reactor core center, experience has shown that the axial flux profile is sufficiently flat so that at least three buckets can be stacked, with negligible variations in neutron exposure. The stacked buckets were laced together with nylon monofilament string. The assembly was lowered to the thimble bottom using monofilament string and then raised a measured height (usually 7.5 in.) for maximum uniform-flux exposure.

The duration of most irradiations was 15 min at maximum reactor power (1 Mw). The irradiated samples then were slowly pulled up the irradiation thimble and transported to a "hot" hood. The 10-ml sample bottles were removed from the irradiation assembly with forceps and monitored. In no case was a sample processed which indicated a surface radiation level greater than 100 mr/hr. The aqueous solutions were thermally warm, and occasionally drops of moisture were observed on the inside of the bottle tops, especially from those sample bottles in the top bucket. By placing a polyethylene cover-disc over the top bucket in the stacked assembly, this appearance of moisture was eliminated. It is felt that the condensation resulted when the warm samples were pulled past cool air in the thimble. The organic samples were somewhat mushy when removed from the reactor, and in many cases they had darkened if they were not already dark before the irradiation.

The irradiated samples were carefully transferred to unirradiated 10-ml bottles to eliminate undesirable activities from the sample bottles and contaminants on their outer surfaces. The bottles containing 5 ml of aqueous solutions were washed with 5 ml of water in small portions to assure complete transfer of all chlorine activity induced in the solutions and to give a final 10-ml volume for radiation counting.

For transferring the solid organic samples, a regular polyethylene bottle top was drilled with an 11/16-in. hole and then screwed one-half tight onto a previously weighed, unirradiated 10-ml polyethylene bottle. After removing the top from an irradiated organic sample container, the container was screwed into the free half of this drilled top so that the open ends of both bottles were flush to each other. The bottom of the irradiated container was cut off with a razor blade and, by means of an 11/16-in.-diameter Teflon rod, the organic was pushed into the weighed receiving bottle. After separating the bottles and stoppering, the organic and aqueous solutions had similar geometries desired for radiation counting. This transfer procedure was rapid, and with 20 min following the end of an irradiation, all samples were ready for analysis. Although most of the terphenyl from each sample bottle was transferred, the counting bottles containing terphenyl later were weighed to give, by difference, the accurate weight of terphenyl actually analyzed. Parts used for sample irradiation and transfer are shown in Figure 1.

C. RADIATION DETECTION

The radiation detection facility consists of two 5- by 5-in. NaI(Tl) crystals mounted face to face on Lucite supports. Each crystal is connected with a photomultiplier tube in a single ("unitized") assembly manufactured by Isotopes, Inc., and at 1050 volts they show a resolution for the 661-keV Cs^{137} gamma photopeak of 7.3%. Between the crystals there is a Lucite block with a 13/16-in.-diameter hole drilled for reproducibly positioning a 10-ml polyethylene bottle. A 3/8-in.-thick aluminum block is attached to each side of this Lucite block to serve as an additional beta absorber. The entire detector assembly is centered in a cave made of 4-in.-thick lead bricks. Its outside dimensions are 28 by 28 by 50 in. and it is lined internally with 0.1-in. cadmium and 0.25-in. aluminum sheet. Samples are inserted into the cave through a plugged hole in the lead top directly above the sample holder.

Two coincidence techniques were used to determine Cl^{38} abundance: ordinary coincidence counting and sum-peak coincidence spectrometry. The former technique⁽⁸⁾ uses two pulse-height selector windows, each for detecting one of the Cl^{38} gammas seen by one of two scintillation crystals and gives a "count" when both windows simultaneously detect. The latter is an integral-bias sum

Figure 2. Ordinary Coincidence Unit

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tube preamplifier, PA,⁽¹⁰⁾ of good stability against temperature changes and count-rate fluctuations is mounted directly on each crystal photomultiplier-tube assembly, X. High voltage, HV, is provided for each photomultiplier tube by a John Fluke Co. regulated power supply Model No. 412A. Output pulses from each preamplifier are directed to the inputs of two Cosmic Radiation Labs, Inc. Model 901 linear non-overloading double-delay-line clipped amplifiers, A. The amplifier prompt outputs are connected to Cosmic Radiation Labs., Inc. Model 901-SCA single channel analyzers, SCA, whose output pulses are sent to (1) the input of a medium-fast coincidence unit, C;⁽¹¹⁾ (2) a Technical Measurement Corp. multichannel analyzer, MCA, ON-gate; and (3) a Cosmic Radiation Labs. Model 1101-S nuclear scaler, S. Whenever a pulse passes through each SCA within the coincidence-unit 120-nsec resolving time, the coincidence unit emits a pulse. This pulse is sent to the input of a scaler for tabulation.

The MCA is used only for setting the SCA windows. The amplifier 2- μ sec delayed outputs are connected to the independent dual inputs of the MCA. With these dual inputs, one-half of the multichannel memory (400 channels) is reserved for pulses entering each input so that it serves essentially as two smaller (200-channel) MCA's. Each half is gated on to receive the delayed amplifier pulses every time its corresponding SCA has an output; consequently, the MCA scope display is of that portion of the sample gamma spectrum passed through an SCA window.

Figure 3. Sum-Peak Coincidence Spectrometer

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The ordinary coincidence counter is readily modified to the sum-peak coincidence spectrometer mode as diagrammed in Figure 3. To accomplish this modification, the amplifier 2- μ sec delayed output pulses are directed to the inputs of a Cosmic Radiation Labs, Inc. Model 1401 Mixer-Adder, and the output pulses from this unit are fed to one input of the MCA. A portion of each amplifier's prompt outputs is selected by the SCA's operated in the integral mode (wide open window) and directed to the coincidence unit whose output is fed to the proper ON-gate of the MCA. The MCA scope display is the sum-peak coincidence spectrum. Removal of the coincidence requirement gives a normal sum spectrometer of $\sim 80\%$ 4π geometry, and further removal of one input to the mixer-adder gives a normal end-window spectrometer.

D. DATA

To calibrate the ordinary coincidence counting system for an analysis, a chlorine standard solution is placed into position, and the SCA windows are adjusted so that the MCA scope shows that the 1.64-Mev Cl^{38} gamma photopeak is passed by one SCA and the 2.16-Mev Cl^{38} gamma photopeak is passed by the other. The windows are made very narrow so that a minimum of activities other than Cl^{38} will be counted.

Standards and unknowns are alternately placed into the cave and counted. The decay of the series of samples irradiated for one analysis is followed for at least two half-lives. Generally, each sample is counted about six times for

1-min periods. Experience has shown that no interferences cause the Cl^{38} decay curve to vary from a straight line so that this is sufficient to establish an accurate estimate of the relative Cl^{38} abundance at some fixed time following irradiation termination. The coincidence background rate is essentially zero; and in most of the runs, the SCA count rates are not large enough to require correction for random coincidence counts.

A least-squares regression analysis is performed on the count-rate data to give a straight-line calibration curve of coincidence count rate, y_i , vs added chlorine, x_i . An estimate of the chlorine content in the unknown, x_j , is obtained by inserting an unknown's coincidence count rate, y_j , into the regression equation.

Two approaches are used to determine the error in x_j . When only one measurement is made on a given sample, the error is computed as follows. First, the variance of estimate, $s^2(\hat{y})$, i.e., the sum of the squares of the deviations between y_i and $\hat{y}_i$ divided by the available degrees of freedom, is calculated. (The statistical symbolism is that described in Reference 12). The $\hat{y}_i$ terms are obtained by substituting the x_i terms into the regression equation, while the available degrees of freedom are $N - 2$, where N is the number of standards used to construct the calibration curve. The square root of $s^2(\hat{y})$ yields the standard deviation of estimate, $s(\hat{y})$.

The standard deviation for any single estimated value, $s(\hat{y}_j)$, determined by substitution of the value for x_j into the regression equation, is given by⁽¹²⁾

$$s(\hat{y}_j) = s(\hat{y}) \left[1 + \frac{1}{N} + \frac{(x_j - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right]^{1/2} \quad \dots (1)$$

where $\bar{x}$ is the average chlorine content of the standards, i.e., $\sum x_i / N$. But when $s(\hat{y}_j)$ is expressed as a percentage of y_j to give the percent relative standard deviation, $100 s(\hat{y}_j) / y_j$, one gets a value which is equivalent to the percent relative standard deviation in x_j ; i.e.,

$$\frac{s(\hat{y}_j)}{y_j} = \frac{s(\hat{x}_j)}{x_j} \quad \dots (2)$$

Therefore, the uncertainty in x_j is $[s(\hat{y}_j)/y_i]x_j$ so that the unknown is reported as containing $x_j \pm s(\hat{x}_j)$ μg of chlorine.

When more than a single analysis is made on a given sample, then the standard deviation is computed from an equal-weight average in the normal manner according to

$$s(\hat{x}_j) = \left[\frac{\sum (x_j - \bar{x}_j)^2}{n - 1} \right]^{1/2}$$

where n is the number of analyses.

III. RESULTS AND DISCUSSION

One of the two techniques of instrumental neutron-activation analysis which is used for detecting a desired activity in a mixture of activities is spectrum stripping. When the desired activity is short-lived, spectra are accumulated in a multichannel analyzer and recorded on magnetic or punched-paper tape. At a later date, the activity of a standard is stripped (i. e., subtracted electronically by means of a computer available with most modern multichannel analyzers) from the unknown mixture to give the relative amount of impurity present.

Figure 4 shows spectra taken at approximately the same time after an irradiation of equal volumes of water and of water to which had been added 1 ppm chlorine as calcium chloride. The Cl^{38} presence is almost obscured in the "pure" water spectrum by other activities, especially Na^{24} . It was found by stripping, however, that 3.5% of the standard spectrum was required to eliminate the photopeak at 1.64 Mev from the water spectrum thereby giving a chlorine concentration for the water of about 35 ppb. The result is inconclusive with just this information as there could be a gamma peak at this energy resulting from some activity other than Cl^{38} ; e. g., it could be an escape peak from a 2.15-Mev Mn^{56} gamma. Such doubts can be eliminated by means of a sum-peak coincidence spectrum.

Figure 5 shows spectra of an irradiated sodium-chloride solution obtained by the spectrometer in the normal sum mode and in the sum-peak coincidence mode. The normal sum spectrum has photopeaks resulting from Na^{24} and Cl^{38} plus additional ones from Ar^{41} , Mn^{56} , and some positron emitter. For the sum-peak coincidence mode with a 10-kev bias on both SCA's, the prominent peaks in the spectra are reduced to only the 1.02-Mev positron annihilation, 3.80-Mev Cl^{38} , and 4.12-Mev Na^{24} sum-peaks. When the SCA bias levels are increased to 1.4 Mev, all peaks are eliminated from the spectra except the 3.80-Mev Cl^{38} sum peak.

Similar spectra of an irradiated terphenyl are shown in Figure 6. These spectra were obtained about 30 min after termination of a 15-min irradiation and are typical spectra for virgin reactor-grade organics. The sum-coincidence requirement suppresses peaks from activities other than Cl^{38} as well as confirms its presence in the sample. When analyzing spectra with sum-peaks, one

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Figure 4. End-Window Gamma-Ray Spectra

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Figure 5. Gamma-Ray Spectra of a Neutron-Activated Sodium-Chloride Solution

Figure 6. Typical Gamma-Ray Spectra of a Neutron-Irradiated Terphenyl

should remember that the apparent sum-peak energy is always more than the calculated energy due to detector nonlinearity.⁽¹³⁾ Thus, the Cl^{38} sum-peak appears at 3.86 Mev rather than 3.80 Mev ($2.16 + 1.64$).

The second instrumental-analysis technique used for detecting a desired activity is decay-following. Activity is recorded as a function of time and identification of the desired activity is accomplished by measuring the half-life. The decay must be followed until the half-life can clearly be established. Comparison of activities for standards and unknowns gives the relative abundance.

Figure 7 shows the gamma decay of an activated sodium-chloride solution obtained from the ordinary coincidence counter, and the gamma decay of a similar sample obtained from one input channel to this counter. The latter data yield a complex decay curve which cannot be resolved accurately unless data are collected for many hours. The curve with half-life labeled "about 40 min" was resolved from that portion of the complex curve shown. On the other hand, coincidence decay follows straight for 10 half-lives of 37.3 min to near background so that an accurate estimate of the Cl^{38} count rate could have been obtained in

Figure 7. Gamma-Ray Decay Curves

1 hr or so. The straight line clearly shows how interferences normally associated with Cl^{38} detection are eliminated by the coincidence counting.

Both coincidence counting techniques allow specific identification of Cl^{38} ; however, more samples can be analyzed during a given time by the decay-following technique and the data obtained are not made bulky with excess information. Consequently, coincidence decay-counting was the primary method for obtaining Cl^{38} abundances, and coincidence spectra were recorded only to confirm Cl^{38} presence when the counting statistics were poor.

Figure 8 shows coincidence decay curves obtained for calibration standards in a typical analysis. Experience has shown that with the experimental conditions used in this study, no interferences cause the decay curve to vary from a straight line so that only a few data points are required for each sample in order to obtain an accurate estimate of the relative Cl^{38} abundance. Note that the statistics are

Figure 8. Typical Cl^{38} Calibration-Standards Decay Curves

somewhat poor for the aqueous blanks and one might suspect that the counts were not actually due to Cl^{38} . In a doubtful case such as this, the sum-peak coincidence spectrum is taken to confirm the Cl^{38} presence.

A typical calibration curve of coincidence count rate, y_i , vs added chlorine, x_i , is shown in Figure 9. The regression analysis of the data used to construct this figure gives an equation whose variance of estimate, $s^2(\hat{y})$, is 447 (coincidence counts/min)² and whose standard deviation of estimate, $s(\hat{y})$ is 21 coincidence counts/min. This latter term, expressed as a percentage of the standard's average coincidence count rate, $\bar{y}$, gives a relative standard deviation of estimate of 7.7%.

Figure 9. Typical Calibration Curve for Chlorine Activation Analysis

TABLE 1
STATISTICAL ANALYSIS OF CALIBRATION DATA USED FOR
DETERMINING CHLORINE IN TERPHENYLS

Analysis Number	$s(\hat{y})$ (c/min)	$\bar{y}$ (c/min)	$100 s(\hat{y})/\bar{y}$ (%)	N Standards	$\bar{x}$ (μ g Cl)	$100 s(\hat{y}_j)/\bar{y}_j$ (%)
1	72	1044	6.9	5	11.0	8.3
2	100	1985	5.0	6	17.5	5.8
3	34	374	9.0	5	3.3	10.8
4	51	591	8.6	6	6.7	10.0
5	52	910	5.7	6	9.6	6.6
6	47	552	8.4	5	6.5	10.1
7	59	740	8.0	8	8.3	9.0
8	10	414	2.4	5	11.5	2.9
9	18	495	3.6	7	4.3	4.1
10	19	437	4.3	7	4.3	4.9
11	21	274	7.7	9	3.9	8.6
12	32	277	11.5	5	6.0	13.8
13	75	857	8.7	5	5.0	10.4
14	45	749	6.0	13	4.0	6.5
15	40	307	13.0	5	15.0	15.6
16	470	3924	12.0	5	7.5	14.4
17	51	335	15.2	5	7.5	18.2
18	270	3798	7.1	5	9.0	8.5
19	1120	6360	17.6	5	7.5	21.1
20	58	666	8.7	7	7.5	10.0

A list of some statistical results determined from the calibration curves of 20 analyses is given in reverse chronological order in Table 1. For each analysis there is given $s(\hat{y})$, $\bar{y}$, percent relative $s(\hat{y})$, N , $\bar{x}$, and percent relative $s(\hat{y}_j)$ for an unknown whose x_j value is equal to the x value. Since the weight of terphenyl which is added to one of the sample containers used is approximately 10 g, one-tenth of the $\bar{x}$ values given in Table 1 gives for each analysis the most accurate unknown's chlorine concentration in parts per million that could have been determined. The relative errors in the last column would be calculated for an unknown which had exactly $\bar{x}$ μg chlorine. For example, if in Analysis No. 1 a 10-g sample had 1.10 ppm chlorine, then in 68 out of 100 analyses the determined value would be between 1.19 and 1.01 ppm chlorine (8.3% of 1.10 is 0.09).

The quantity of chlorine which can be determined most accurately from a calibration curve is that amount equivalent to $\bar{x}$ (see Equation 1). For this reason, it is advisable to have the standard's chlorine content uniformly bracket the unknown's, i. e., $\bar{x} = x_j$. Although the uncertainty will be greater whenever the chlorine in the unknown is not $\bar{x}$ μg , the increase will not be too great for amounts of chlorine falling in the range of values used to construct the calibration curve if the relative standard deviation of estimate is low. Therefore, one can conservatively estimate from recent results in Table 1 that chlorine can be determined in the 0.4- to 2-ppm range in terphenyls with a standard deviation of about 7%.

Some results of analyses for chlorine by the gamma-gamma coincidence counting method are listed in Table 2. Several samples were taken from batches of each of the materials listed. The organics in the first three columns were virgin terphenyls, whereas the other materials were irradiated terphenyls which had been removed from a nuclear reactor. The range in values of the determinations for samples taken from one material may result from the inherent accuracy of the technique and/or from inhomogeneities of the materials sampled. The latter is especially suspect for the materials labeled OC859 and OC1119. These organics were received as large chunks of material which appeared rather nonuniform. The agreement between determinations is best for the homogeneous liquid material 21. The ~2-ppm values determined for the virgin materials are typical for the reactor-grade organics analyzed in this laboratory for the past

TABLE 2
CHLORINE CONCENTRATION (ppm) OF SOME TERPHENYL SAMPLES

Sample Number	Terphenyl Designation					
	AE3BT*	AB125†	AB99†	OC859§	OC1119§	21**
1	2.07	2.85	2.00	0.082	0.20	0.99
2	2.05	2.48	1.79	0.092	0.17	0.92
3	2.22	2.87	1.67	0.106	0.23	0.98
4	2.42	2.79	1.82	0.100	0.27	—
5	2.43	2.86	1.93	—	0.22	—
6	—	3.01	—	—	—	—
Av. $\pm \sigma$	2.24 $\pm$ 0.18	2.81 $\pm$ 0.17	1.84 $\pm$ 0.13	0.095 $\pm$ 0.010	0.22 $\pm$ 0.04	0.96 $\pm$ 0.04
Relative σ (%)	8.0	6.0	7.1	11	16	4.2

*Virgin Santowax OM — an ortho- and meta-terphenyl mixture

†Virgin Santowax OMP — an ortho-, meta-, and para-terphenyl mixture

§Irradiated Santowax OMP taken from Piqua Nuclear Power Facility (PNPF), Piqua, Ohio

**Irradiated Santowax OM taken from U-3 loop at NRU, Chalk River, Ontario, Canada

2 yr. The thermal environment and nuclear irradiation of these materials is expected to reduce the chlorine content, and that is found to be the case as indicated by the other results listed in Table 2.

Since some chlorine impurity might be volatile, attempts were made to distill chlorine from samples prior to analysis. The results of this investigation are listed in Table 3. The material analyzed was from a batch of virgin Santowax OMP received as finely cut flakes. Samples 1, 3, and 4 were pressed into sample containers for irradiation, whereas the others were melted and then poured into sample containers. Samples 5 and 6 were taken from one melt, but 5 was poured as soon as the material became viscous while 6 was poured at least 5 min later when the melt was fuming steadily. It does appear chlorine can be lost from heating so one must be aware of this possibility when preparing a sample for analysis.

Table 4 shows results of an investigation to determine if any chlorine is lost from thermal heating during irradiation. Such losses have been reported for chlorine analysis of liquid organics.⁽²⁾ Samples were carefully transferred to clean containers following irradiation and analyzed. Then, after most of the induced activities had decayed, the samples were reirradiated for repeat analysis.

TABLE 3
EFFECT OF SAMPLE PREPARATION ON THE
CHLORINE CONCENTRATION IN A
TERPHENYL

Sample Number	Sample Preparation	Chlorine (ppm)
AB125-1	Packed	2.58 ± 0.12
AB125-2	Melted	1.93 ± 0.13
AB125-3	Packed	2.71 ± 0.17
AB125-4	Packed	2.86 ± 0.15
AB125-5	Just melted	3.01 ± 0.13
AB125-6	Melted in 5 min	1.70 ± 0.11

TABLE 4
CHLORINE CONCENTRATION (ppm) OF TERPHENYL
SAMPLES ANALYZED REPETITIVELY

Sample Number	First Analysis	First Re-analysis	Second Re-analysis	Third Re-analysis	Sample Form
AB99-1	2.02 ± 0.11	1.94 ± 0.10	1.94 ± 0.15	1.81 ± 0.09	Solid
AB99-2	1.84 ± 0.10	1.72 ± 0.09	1.94 ± 0.14	1.77 ± 0.08	Solid
AB99-3	2.16 ± 0.17	1.85 ± 0.12	—	—	Solid
21-1	1.07 ± 0.04	0.91 ± 0.07	—	—	Liquid
21-2	0.92 ± 0.04	0.96 ± 0.07	—	—	Liquid
AB125-1	2.48 ± 0.18	2.87 ± 0.12	2.79 ± 0.20	—	Solid
AB125-2	1.94 ± 0.15	1.92 ± 0.10	—	—	Solid

Special care was taken not to introduce chlorine from one run to the next. There does not appear to be a significant loss, if any, in chlorine content at this concentration range in either the solid or liquid samples.

Two batches of organics were spiked with various weights of triphenyl tin chloride in order to give series of organics with a range of chlorine concentration. Chlorine determinations were made on these samples and the results are plotted vs chlorine added in Figure 10. The lines drawn through the data points have unit slopes and the good correlation between the lines and the points further suggests that no significant chlorine loss occurs during the irradiation or processing steps, at least up to about 7-ppm chlorine. The intercepts give organic blank chlorine concentrations of 2.0 and 0.18 ppm, which are typical values for these types of samples. The correlation, in addition, justifies the use of aqueous chloride standard solutions for determining chlorine in organics.

Figure 10. Chlorine Analysis of Terphenyls with Triphenyl Tin Chloride Added

Similar chlorine-spiked organics have been analyzed in this laboratory by x-ray fluorescence methods in attempts to compare results with those obtained by the activation-analysis method. The x-ray fluorescence method gives a linear relationship between instrument response and amount of chlorine added to the

organic over a range from 100-ppm added chlorine down to about 5-ppm added chlorine, but then the instrument response begins to scatter. The estimated standard deviation at the 5-ppm level is 10% and it rises rapidly for samples less concentrated in chlorine. The shorter analysis time required for samples determined by x-ray fluorescence might justify its use for analysis of concentrated samples; however, the activation-analysis results are much superior when chlorine content is below 5 ppm. Samples are limited to less than a few hundred milligrams weight when analyzed by x-ray fluorescence, compared to about 10 g when analyzed by activation analysis. Depending on the amount of material available, this may be an advantage or a disadvantage.

Table 5 gives some results for chlorine determination of the water blank used to dissolve standards. The values were obtained from least-squares calibration-line equations used in 10 chlorine activation analyses. The uncertainty is large (~36%) at this low concentration level, but a great deal of the spread in results may be real since introduction of chlorine at the ppb level is difficult to avoid. Conductivity water has been obtained and will be used for dissolving standards

TABLE 5
CHLORINE CONCENTRATION
OF DEIONIZED-DISTILLED
WATER

Analysis Number	Chlorine (ppb)
1	29
2	13
3	20
4	10
5	33
6	23
7	32
8	25
9	17
10	16
Average Value	22 ± 8

for future analyses. Analysis of this material also shows the presence of chlorine and values of 4, 8, 8, and 14 ppb have been obtained by sum-peak spectrometry and spectrum stripping. If conductivity water is not readily available, then the price does not warrant its use since the effect of the blank can be corrected and it is not likely that samples will be obtained which have any less chlorine present.

IV. CONCLUSIONS

It has been shown that gamma-gamma coincidence techniques, especially sum-peak coincidence spectrometry and coincidence decay-following, can be used for establishing with certainty the presence of relative abundance of Cl^{38} when occurring in a mixture of radioactivities. This accomplishment has permitted the development of a new method for chlorine analysis in organics by neutron activation. The decay-following technique is more suitable for routine analyses. The sum-peak method is used to establish the presence of chlorine at very low levels.

By the new method one can determine chlorine in the 0.4- to 2-ppm range with a standard deviation of about 7% and down to about 10 ppb with a standard deviation of about 50%. These precision and accuracy levels seem to be significantly better than those previously obtainable, and the experimental sensitivity for chlorine detection has been extended to a level that is much below the chlorine-impurity concentration range presently found in organic reactor coolants.

Large samples must be irradiated in order to give sufficient chlorine activity to be observed by coincidence counting; however, this permits a more representative estimate of the chlorine content of the batch sampled.

It was demonstrated that at least up to 7 ppm chlorine in terphenyls, no significant loss of chlorine from the terphenyl occurs due to the activation step of the analysis; and it was shown that the sampling technique can influence results, especially at a few ppm chlorine concentrations.

The analysis was extended to the determination of chlorine in water. Some deionized-distilled water was analyzed at 22 ± 8 ppb chlorine and some conductivity water was shown to have a few ppb chlorine.

The method has been refined to a point where it is now routine in this laboratory. Typically, six determinations can be completed in one work day.

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