

extent of reaction may be measured subsequently at a single fixed time. The data collected then permit simultaneous solution of the proportional equations to yield the initial concentrations of the two components. Techniques of this type may be quite useful for continuous monitoring of industrial processes. Similarly, composites of k and t —i.e., k_1 and t_1 , k_2 and t_2 for a two component mixture—may be used.

Just as the optimum values of time are found by plotting the kinetic term as a function of time, optimum values of the k variable are obtained in an analogous manner from a plot of the kinetic term as a function of the magnitude of the chosen variable. Because the use of variables other than time broadens the scope and extends the versatility of

kinetic methods, their use should be given serious consideration in developing new analytical procedures.

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Iron-55 X-Ray Absorption Analysis of Organically Bound Chlorine Using Conventional Proportional Counting Facilities

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► Modified iron-55 x-ray absorption techniques incorporating conventional proportional counting facilities permit nondestructive analysis of chlorine in a variety of organic materials with good precision and speed. Variations in the technique permit analyses over a wide concentration range. Application of the method as described is limited to technical grade and finished products.

CLASSICAL methods of analysis for total chlorine usually involve some form of sample combustion followed by titration for chloride ion. Besides being time-consuming and destructive of the sample, such methods are susceptible to inadvertent sample handling error.

In 1954, Hughes and Wilczewski reported a simple, rapid, nondestructive x-ray absorption technique for determining a single high atomic number element in lower atomic number matrix material (1). Called *K*-capture spectroscopy, the method utilizes isotopic iron-55 as the source of x-radiation. The method has been applied specifically to determine sulfur in liquid hydrocarbons. Later workers using similar facilities extended the procedure to determination of chlorine and bromine in difficultly soluble solid organic samples (2).

Preliminary examination of the basic technique in this laboratory for determination of total chlorine in organic materials suggested that method utility could be enhanced with certain modifications, particularly in apparatus. Accordingly, such changes have included incorporation of a proportional counting assembly for high-speed counting, which improved precision and reduced analysis time; a thin-window flow type detector for long-term detector stability; and conventional shielded shelf-type mount to hold detector, source, and sample cell at fixed reproducible geometry and to permit general counting flexibility.

THEORETICAL CONSIDERATIONS

Iron-55 decays by *K*-electron capture to stable manganese-55 with the attendant emission of soft *K*-line x-rays of manganese, having an effective wavelength of about 2.05 Å. (0.0059 m.e.v.). Since iron-55 has a fairly long half life of 2.94 years, the isotope is a convenient and safe source of monoenergetic soft x-radiation for analytical use.

The absorption of a narrow beam of monoenergetic x-rays passing through a homogeneous, isotropic sample follows Beer's law. In general, the degree of absorption of incident radiation passing through a given material of given thickness increases with decreasing radiant

energy. Likewise, the degree of absorption of incident radiation of given energy varies with the atomic number of the absorbing material. The absorption of soft x-radiation from iron-55 decay increases markedly with the atomic number of the absorber, as shown in Figure 1. The mass absorption coefficient of chlorine, expressed as square centimeters per gram, is 102 as compared with 0.2, 4.5, and 11.4 for hydrogen, carbon, and oxygen, respectively. This wide margin in absorptivity provides the basis for analysis of a single high atomic number element, such as chlorine, in lower atomic number matrix material.

OUTLINE OF METHOD

The method involves passing a beam of soft x-rays through the sample material supported at fixed, reproducible geometry between the iron-55 source and the detector, measuring the intensity of the transmitted radiation by conventional proportional counting facilities, and relating the logarithm of the transmitted x-ray count rate to the chlorine concentration by reference to a calibration curve for identical amounts of matrix material of known chlorine content.

APPARATUS

Iron-55 Radiation Source. Isotopic iron-55 of 4-mc. intensity was purchased from the Oak Ridge National

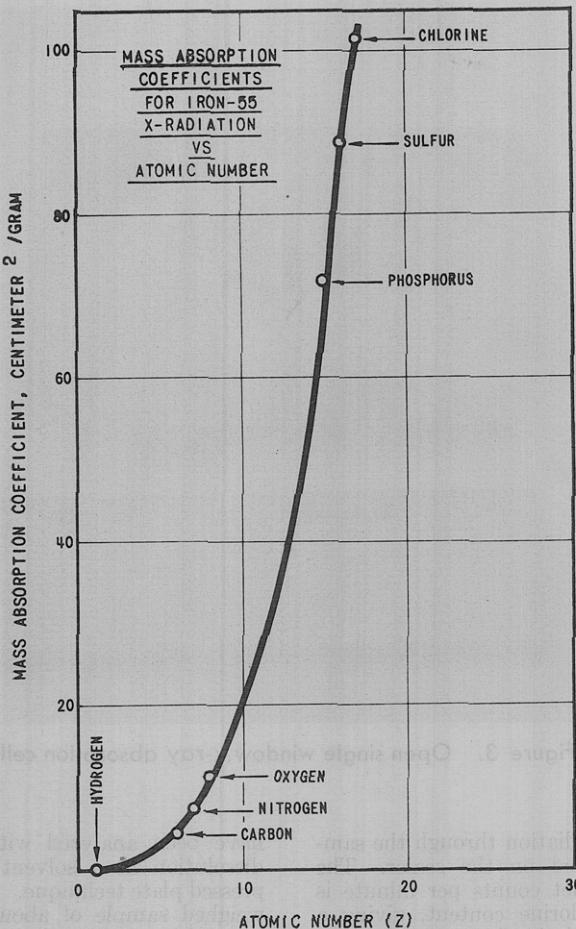


Figure 1. Mass absorption coefficients for iron-55 x-radiation vs. atomic number

Laboratory, Oak Ridge, Tenn., in the form of active ferric chloride in hydrochloric acid solution. An Atomic Energy Commission By-Product Materials License is required for procurement of the material. A sealed source was fabricated in this laboratory by evaporating the solution to dryness within a 1-inch diameter stainless steel counting cup and then covering the active deposit with a thin layer of liquid epoxy resin containing a curing agent. The resulting source is practically indestructible under ordinary handling conditions.

The counting cup containing the source is glued to the center of a $3\frac{1}{4} \times 2\frac{1}{2}$ inch rectangular metal shelf capable of sliding securely into the lucite sample holder described below.

Sample Cells. Horizontal absorption cells with beryllium windows are generally used. The beryllium was purchased as metallic disks from the Brush Beryllium Corp., Cleveland, Ohio. Two cell designs are available to accommodate different types of sample material. For determination of volatile liquids a closed dural-bodied cell with dual windows is used (Figure 2). Internal cell thickness is approximately 4 mm. During sample analysis, the cell is centrally supported above the radiation source within the counting chamber by a rectangular metal shelf from which a central disk of $1\frac{1}{4}$ -inch diameter has been removed.

An open, single window cell of the type shown in Figure 3 is used for analysis of solids or of nonvolatile liquids. The cell body was machined from a $1\frac{1}{2}$ -inch thick aluminum plate to shelf dimensions compatible with the lucite sample holder described below. The cell proper is a 1-inch diameter hole drilled into the center of the plate and sealed at the bottom by a $1\frac{1}{4}$ -inch diameter beryllium window cemented to the cell body with epoxy adhesive. The total available cell depth is approximately 12 mm., which is more than adequate for filling the cell to the maximum sample thickness normally required. As explained below, sufficient sample is accurately weighed into the cell to obtain reproducibly any desired sample thickness for measurement.

Counting Facilities. The counting apparatus is a Baird-Atomic, Inc. (Cambridge, Mass.), university series proportional counting system consisting of Model 800D shielded counting chamber, Model 821R detector, and lucite sample holder assembly, and Model 4125 scaler assembly. The counting chamber houses the detector and sample holder. The detector is a window flow type with a microthin (0.7 mg. per square centimeter) gold coated Mylar end window. The detector is attached to the top of the sample holder, which in turn is fastened to the lower section of the shield. The sample holder is slotted for five different

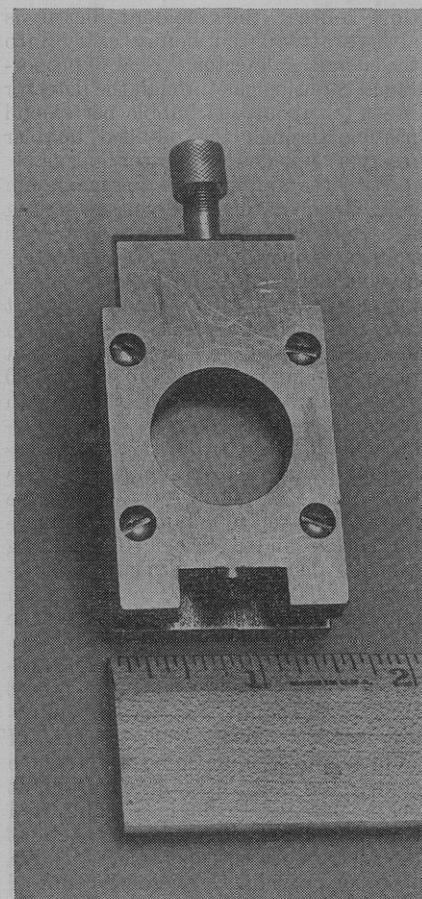


Figure 2. Closed dual window x-ray absorption cell (cell compartment beneath window)

sliding shelf positions for supporting the radiation source, the sample absorption cell, and the detector at fixed, reproducible geometry.

The proportional counting gas for the detector is a mixture of 90% argon-10% methane (P-10 counting gas), supplied by the Matheson Chemical Co., East Rutherford, N.J. Although pure methane can be used in proportional counting, the argon mixture is preferred for the present application because of its approximately twentyfold advantage in detection sensitivity for soft x-rays.

The scaler assembly consists of electronic scaler, electronic timer, non-overloading amplifier, and high voltage supply.

Although not absolutely essential, additional useful counting accessories include calibrated sets of aluminum absorbers supported on rectangular shelves with dimensions compatible with the lucite sample holder. These are available from Radiation Counter Laboratories, Skokie, Ill.

PROCEDURE

Instrument Adjustment. The instrument is adjusted for counting with the source on one of the lower shelves of the sample holder and with a calibrated aluminum absorber on one of the upper shelves between the source and the detector. Because of the relatively high intensity of the radia-

tion source, the incident beam is always attenuated before entry into the energized detector. Flow of proportional counting gas through the detector is set for about one bubble per second passing through the oil-filled bubbler reservoir outside the detector housing.

With the amplifier set for maximum gain, the operating high voltage setting is determined as follows. The high voltage is increased by approximately 50-volt increments, and the corresponding count rate is noted. The count rate will at first increase sharply with increased applied voltage, will reach a plateau spanning a range of 100 or 200 volts, then will finally rise sharply with further increase in voltage. The operating voltage is set within the lower one-half of the plateau region to stabilize the count rate during possible voltage fluctuations and to minimize instrumental background. With P-10 counting gas, the plateau will normally fall between 2400 and 2700 volts. With pure methane as the counting gas, the plateau occurs around 4000 volts.

Measurement of Transmitted Radiation. The scaler provides for preset time, preset count, and manual counting modes. With each series of counting determinations, a reference count for the attenuated radiant beam passing through a calibrated thin aluminum absorber is taken at the instrument settings selected. An absorber providing a reference count of approximately 100,000 c.p.m. is used. This count serves as a routine check on instrument stability and on source decay.

During sample analysis, a minimum of 100,000 total counts are accumulated for good counting precision. The usual counting time required is less than 3 minutes. The gross count rate for transmitted x-rays plus background is obtained by dividing the total number of accumulated counts by counting time. The background count rate, described below, is subtracted from the gross count rate to obtain the net count rate for x-ray transmittance.

Determination of Background. In addition to background of instrumental and cosmic origin, some gamma emission from source contaminants contributes to the observed count. Iron-55 obtained from the Oak Ridge National Laboratory contains a small amount of 1.29 m.e.v., 46-day half life, gamma emitting iron-59, and possibly a cobalt isotope. The total background is determined by noting the count rate with a heavy lead absorber inserted between source and detector at the same shelf position used for the sample absorption cell. The lead absorbs all x-rays but transmits most of the gamma rays to be counted.

Preparation of Calibration Curves. Individual calibration curves are prepared for each type of sample material to be analyzed. Identical amounts of a given base stock material of known chlorine concentration contained in an appropriate absorption cell are placed in a position of fixed reproducible geometry between the source and detector, and the

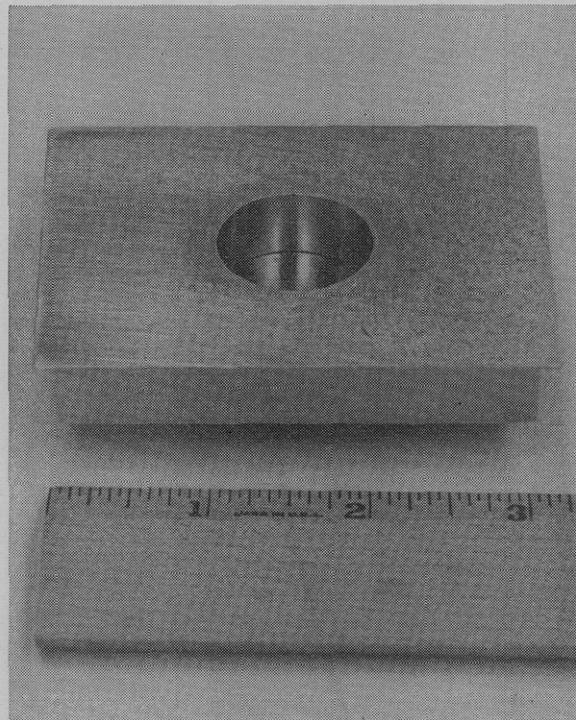


Figure 3. Open single window x-ray absorption cell

transmitted radiation through the sample is registered on the scaler. The logarithm of net counts per minute is plotted *vs.* chlorine content, giving a straight line relationship. A minimum of three data points falling on a straight line is used in preparing the working curve. The required calibration frequency for a given analysis is on the order of 2-week intervals when source decay is the only factor affecting the validity of the calibration.

The amount of base stock material used for analysis is the maximum which will permit good counting statistics within about 3 minutes counting time over the chlorine concentration range to be determined. Sample materials of such high chlorine content as to prohibit direct analysis are diluted with a compatible nonchlorine containing solvent to a suitably low chlorine concentration for precise counting.

Sample Handling. X-ray transmittance measurements are usually made with the sample contained in one of the two types of absorption cells described above. Volatile liquids are analyzed in the closed, dual-window cell. In filling this cell, precautions must be taken to avoid trapping air bubbles in the sample space and to avoid temperature differences of more than 1 or 2 degrees between the sample materials analyzed and the calibration standards used to prepare the working curves.

Samples of nonvolatile liquids or of solids dissolved in a nonvolatile liquid may be analyzed either in the closed cell or in the single window open type of cell. The open cell is filled reproducibly by accurately weighing the liquid sample into the center of the cell and allowing the liquid to distribute itself uniformly.

To a limited extent, solid samples

have been analyzed without previous dissolution in a solvent by use of a pressed plate technique. An accurately weighed sample of about 0.3 gram is pressed into a $\frac{1}{2}$ -inch diameter plate at 30,000 p.s.i.g., using a Pasadena Hydraulics Laboratory press and the standard $\frac{1}{2}$ -inch die normally used for preparing potassium bromide pressed plates. The pressed sample disk is centered above a $\frac{1}{4}$ -inch aperture drilled into the center of a rectangular lead shelf placed in the sample holder between source and detector. This arrangement enhances geometrical reproducibility by permitting only a narrow beam of radiation to pass through a small area of the sample while preventing any radiation not passing through the sample from reaching the detector.

RESULTS AND DISCUSSION

Precision and Accuracy. The major errors inherent in the method as applied are errors contributed by counting statistics, nonreproducible geometry in the counting arrangement, and variations in base stock composition of sample material.

All other factors being equal, method precision is limited ultimately by the statistics of counting. The standard deviation in counts for any single reading is equal to the square root of the total number of counts accumulated, which, in turn, depends upon count rate and counting time. Since the percentage error decreases with increasing number of counts recorded during a given determination, the statistical error in the present applications was minimized consistent with reasonable sample count rates and counting time. During each

analysis 100,000 total counts were accumulated, thus limiting the standard error in counting rate to around 0.3%.

All comparative counting determinations must be carried out under exactly reproducible conditions of geometry. Variations in the vertical and horizontal relationship of the source, sample cell, and detector to one another must be minimized.

Variations in base stock composition—i.e., changes in the normal proportions of low atomic number matrix elements—and in density from sample to sample will affect the accuracy of results obtained by use of the working curve. Accordingly, the method has been applied only to the analysis of technical grade and finished products.

The x-ray method was applied to the determination of chlorine in a large number and variety of organic samples, and the results were then compared with those obtained by the conventional bomb combustion-titration procedure. As shown in Table I, the agreement between the two methods was generally within the standard deviations of the results. Experience in this laboratory has shown the x-ray absorption technique to be more reliable because of minimized sample handling and minimized inadvertent sample contamination.

The minimum concentration of chlorine detectable by x-ray absorption is around 0.01%. For the analysis of homogeneous liquid samples, results are normally accurate to within $\pm 0.02\%$ chlorine at concentrations below 0.5%.

At concentrations in the 10% range, an accuracy to within $\pm 0.2\%$ chlorine can be expected.

The pressed-plate, solid-sampling technique suffers in precision because of difficulty in reproducing sample geometry exactly. Normal variations in geometry limit the analytical precision to about $\pm 0.05\%$ chlorine at concentrations below 0.5%. Since the sensitivity advantage of direct solid sample analysis is offset by geometrical imprecision, solid samples are preferably analyzed after dissolving them in a suitable solvent. Whenever possible, a solvent is used which contains the low atomic number matrix elements in approximately the same proportions as does the sample material being analyzed.

Speed. The usual time of analysis, including sample preparation, counting, and calculation of results is less than 5 minutes. Because of the high counting rates attainable by proportional counting without detector resolution losses, the counting time required for a given statistical counting precision is only a fraction of that required by Geiger counting. The advantages of higher speed counting for ultimate analytical precision appear to outweigh the marginal gain in sensitivity which is obtained by increasing sample size.

Cost. The cost of the facilities described, including radioactive source, is on the order of \$2500. This is less than the cost of a commercial version of the less flexible apparatus described by earlier workers.

Table I. Comparative Chlorine Analyses^a

Iron-55 X-Ray	Combustion-Titration
0.02 \pm 0.01	0.02 \pm 0.01
0.03 \pm 0.01	0.04 \pm 0.01
0.08 \pm 0.01	0.10 \pm 0.01
0.23 \pm 0.01	0.21 \pm 0.01
0.50 \pm 0.02	0.45 \pm 0.02
1.05 \pm 0.03	1.00 \pm 0.02
9.6 \pm 0.2	9.4 \pm 0.1

^a Weight per cent.

Radiation Safety. The installation described presents no radiation hazard, provided normal handling precautions are followed. The only appreciable radiation is directed upward in a conical beam from the source. Horizontal radiation toward the operator is absorbed by the sides of the counting cup holding the source. The removable shelves can be easily manipulated in and out of the counting chamber without exposure to the radiant beam. The heavy door of the shield is normally closed except during sample changing.

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Determination of Niobium and Tantalum in Minerals, Ores, and Concentrates Using Ion Exchange

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► The hydrochloric-hydrofluoric acid system was found suitable for the determination of niobium and tantalum in various minerals and ores by ion exchange procedures. No preliminary separations are required, and the ion exchange steps provide clean-cut separations from virtually all elements with which niobium and tantalum are associated. Tin, antimony, and bismuth require minor modifications of the procedure. The decomposition of the sample depends to some degree on its composition; a hydrochloric-hydrofluoric acid attack under light pressure is suitable in most instances.

Of the niobium and tantalum bearing minerals, columbite and tantalite ($\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$) are most important. Depending on the origin, these minerals are contaminated with varying amounts of titanium, tin, zirconium, calcium, and tungsten.

Since the amount of available columbite/tantalite ore is limited, increasing amounts of pyrochlore, $\text{NaCaNb}_2\text{O}_6$, and microlite, $(\text{NaCa})_2\text{Ta}_2\text{O}_6(\text{O}, \text{OH}, \text{F})$, are being processed which, besides other calcium bearing minerals, frequently contain some rare earths. Simpsonite, $\text{Al}_2\text{Ta}_2\text{O}_8$, is also being used while the rarer euxenite, $(\text{Y}, \text{Ca}, \text{Ce}, \text{U}, \text{Th})$ -

$(\text{Nb}, \text{Ta}, \text{Ti})_2\text{O}_6$ and samarskite, $(\text{Y}, \text{Er}, -\text{Ce}, \text{U}, \text{Ca}, \text{Fe}, \text{Pb}, \text{Th})(\text{Nb}, \text{Ta}, \text{Ti}, \text{Sm})_2\text{O}_6$, because of their high uranium content, are desirable only if a recovery of the uranium is also envisaged.

A comprehensive review of methods available for the analysis of niobium and tantalum bearing ores and concentrates was published in 1952 (1). Most methods represented modifications of the original Schoeller procedure (28, 30, 31, 36), which is based on a preliminary collection of the combined oxides of niobium, tantalum, titanium, zirconium possibly contaminated by tungsten and phosphorus. After removal of titanium