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X-RAY ABSORPTION AS AN ANALYTICAL TOOL IN NUCLEAR CHEMISTRY

by

C.J. TOUSSAINT

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possibilities, in respect to X-ray diffraction and X-ray fluorescence analysis,
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In this report the different kinds of absorption techniques are described,
each technique is followed by some applications concerning particularly the nuclear
chemistry field.

Among the different absorption analysis methods such as : the fine structure determination of absorption spectra of the nuclides (a more fundamental investigation) and the absorption-fluorescence method for the determination of cladding thickness of nuclear fuel elements, the absorption-edge method is the most interesting for our problems.

This method has first of all the great advantage of a relative freedom from both direct and matrix interferences. Secondarily it is a non-destructive method and thirdly a wide range of elements can be determined from chromium onwards, in the table of atomic numbers.

Precision and accuracy of the method are fairly good. The determination of each element requires generally from 15 minutes to 1 hour, with a dissolved sample, and only a small amount of solution is needed (0.2-2 ml.).

Disadvantages arise from the limit of concentration which can be determined (generally 0.05 g/l).

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SUMMARY

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In this report the different kinds of absorption techniques are described, each technique is followed by some applications concerning particularly the nuclear chemistry field.

Among the different absorption analysis methods such as : the fine structure determination of absorption spectra of the nuclides (a more fundamental investigation) and the absorption-fluorescence method for the determination of cladding thickness of nuclear fuel elements, the absorption-edge method is the most interesting for our problems.

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Precision and accuracy of the method are fairly good. The determination of each element requires generally from 15 minutes to 1 hour, with a dissolved sample, and only a small amount of solution is needed (0.2-2 ml.).

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1 — INTRODUCTION

When an X-ray beam passes through a thin layer of matter, the following equation is valid:

$$I = I_0 . e^{-\mu_m . f . x} = I_0 . e^{-\mu_m . G}.$$

Where μ_M = the mass absorption coefficient

f = the density of the sample in g/cm^3

$G = fx$ = the mass thickness of the sample in g/cm^2

For a given element the mass absorption coefficient may be expressed empirically as a function of wavelength by an equation having the following form [1].

$$\mu_M = C \lambda^n Z^m + b (c)$$

in which :

C = a constant for a given element in a given wavelength range

λ = wavelength

Z = atomic number of the element

b = expression for the scattering and also a function of λ and Z

n = varies between 2.5 and 3.0

m = approximately 4

Generally it is possible to subdivide the absorption techniques in the following way :

— FINE STRUCTURE

— ABSORPTIOMETRY WITH POLYCHROMATIC BEAMS

    — X-ray photometer analysis

    — Absorption-fluorescence technique

— ABSORPTIOMETRY WITH MONOCHROMATIC BEAMS

    — Simple absorptiometry

    — Modified differential absorptiometry

    — Absorption-edge method

2 — FINE STRUCTURE

Determination of the fine structure of X-ray absorption spectra has become of growing importance during the last years in analytical chemistry. This because the change of wavelength of the absorption-edges is related to the chemical binding of the substances ([2, 3, 4]). K. Tsutsumi([5]) for instance found a close relationship to the crystalline or molecular state, studying the fine structures of the K-absorption spectra of metallic cobalt, and iron, the latter in the form of ferrous-ammoniumsulphatehexahydrate. Further Zemany ([6]) showed that the chemical state of an element can affect the structure and position of the absorption edge and both the wave-length and intensity of an emission line. He proposed for instance to use the latter phenomena to determine the valence state of manganese in various crystalline modifications or in alloys by the shift in position of the K/B line using a conventional spectrograph.

Much fundamental work has been done by Y. Cauchois ([7, 8]). Some very interesting articles are her study of the K-absorption spectra of metallic nickel, arsenic, gallium, ([9]) and metallic aluminium ([10]), using a special spectrometer with photographic plates instead of detectors.

Menescu ([11]) at least found a correlation between the displacement of the L_{III} edge of rhenium ([12]), and the L_I, L_{II}, L_{III} edge of uranium, with the degree of oxidation of these metals.

But at present only little work has been done in the field of the nucleonics.

3 — ABSORPTIOMETRY WITH POLYCHROMATIC BEAMS

Absorptiometry with polychromatic beams, is analogous to colorimetry with white light. Analytical methods based on this method are rapid, non-destructive and very sensitive, when the desired constituent is of a considerable atomic number higher than the other elements present.

Probably the most serious disadvantage is nonspecificity, as all elements absorb X-rays to some extent. Furthermore polychromatic beams are not generally narrow and may be divergent, so that the beam reaching the detector can consequently include X-rays generated in the sample and different portions of the beam may have traversed slightly different lengths of sample.

This technique appears to greatest advantage in the kinds of applications as radiography ([13]) non-destructive testing of materials ([14]) and thickness determination ([15]), in which a high beam intensity is extremely desirable as it tends to shorten the time required for observation and to make simple equipment. Also gases lend themselves well to absorptiometry with polychromatic beams ([16]). The fact that gases have a simple equation of state, makes possible the use of absorptiometry with polychromatic beams to give information about the state of a gas under conditions transient or difficult of access for instance in detonation waves ([17]), boundary layers ([18]) or supersonic flow ([19]). Temperature measurements have also been made ([20]). The technique is a unique method for studying the fluidization of a finely divided solid by a gas([21a]). Bad density profiles, which reveal the character and fluidization effectiveness have been readily determinated, without disturbing the system as probes would inevitably do ([21h]).

Finally X-ray absorptiometry with polychromatic beams establishes not only the average composition of a material, but also its lack of uniformity as well.

3.1 — X-ray photometer analysis

To measure and convert X-ray absorption to chemical concentrations, by the photometer analysis there are four different methods ([22]).

3.1.1 — Normal technique

By this method the sample solution is placed in one of the X-ray beams and its absorption is matched by placing calibrated aluminium blocks plus a portion of the tapered aluminium attenator disk in the other beam, so that the absorption by the sample is matched entirely with the required thickness of aluminium metal. This is the simplest technique from the point of view of the number of standard solutions needed for a calibration and the range of concentration to which a simple calibration curve can be applied. But this technique is also the least precise. Errors arise from :

a) fluctuations of line-voltage because of the unequal change in absorption of harder or softer X-rays by the sample in the aluminium standard

b) fluctuations of temperature, because of the change in density of the sample solution

c) improper adjustments of the instrument controls.

The latter may result in a slight change in slope of the absorption curve and deviations from the original calibration curve may become appreciable at considerable distance from the origin; i.e. at high absorptions.

3.1.2 — Differential Technique

Precision is improved by the use of differential technique in which the absorption of a sample is matched in large part by the absorption of standard reference solution of similar composition, only a small thickness of the aluminium attenator disk being required to complete the balance. One advantage of measuring only a small difference between the absorptions of two solutions is that errors caused by temperature fluctuations are minimized, since the densities of the sample and the reference solution vary in a similar matter. A second advantage is that no errors result from fluctuations in line-voltage when both X-ray beams traverse similar absorbants.

A third advantage is that errors arising from incorrect adjustments of the instrument controls are smaller, since the calibration curve is tied to a standard reference solution and not to a given instrument setting alone. This technique however, requires a large number of standard solutions to calibrate over a wide range of absorption, but this is compensated by the fact that all calibration curves are straight lines. if the absorption range for each reference solution is not too great.

3.1.3 — Cris-Cross Differential Technique

The highest precision has been achieved with a technique called the criss-cross differential technique ([23]). Here an aluminium tape is placed permanently in the righthand beam in order to permit measurements of solutions having smaller concentrations than that of the solution in the standard beam.

One instrument reading is made with the sample in one of the X-ray beams, and the reference solution in the other. A second measurement is made after switching positions of the two cells. Corrections for any extraneous substances that may be present, are substracted from the reading obtained with the sample on the left side. The solute concentration is then determined by the appropriate calibration curve, one curve having a positive slope, the other a negative one. This technique minimized instrumental errors and experimental results showed that this technique gave more absolute precision.

3.1.4. — Direct Comparison Technique

When an extremely accurate and precise analysis is required, the direct comparison method is used. In this method the total absorption of the sample and of a standard sample of nearly identical concentrations are measured at the same time and against the same reference solution. The concentration of the unknown is computed directly from the value of the standard solution and the slope of the absorption curve. But as the method is only valid when the concentrations of the sample and standard are nearly identical, it has only a very limited and specialized application.

Applications

M.C. Lambert ([24]) determinated uranium in solution and found, by using a 12 mm cell path length for a solution containing 50 g of uranium per liter, for the normal method, a precision of $\pm$ 0.18 g/liter or $\pm$ 0.36%. With a 1 mm path length and a solution containing 500 g/l, the precision was $\pm$ 1.7 g/l or $\pm$ 0.34%.

He found thus, that when it was necessary to measure the absorption of very strong solutions directly, in order to avoid the troubles of automatic dilution in the case of inline analysis of concentrated process streams, it was possible to decrease the cell path length without an appreciable effect on precision. Lambert ([25]) also measured uranium in solution by the different techniques. The different in precision, is very well illustrated in table 1.

TABLE 1

Method	Concentration Range g/liter	Precision 99% confidence limit
Normal Technique	5—10	$\pm$ 1.3%
	10—35	$\pm$ 1.0%
	35—55	$\pm$ 0.7%
Differential Technique	40	$\pm$ 0.4%
Criss-Cross Diff. Technique	30—42	$\pm$ 0.25%

Bartlett T.W. ([26,27]) determinated uranium in uranyl-nitrate solutions containing 0.07-90 g of uranium per liter. In the lower part of this range up to 10 g/l, the limit of error per reading on the 95% confidence level was $\pm$ 0,05% of uranium per liter. With the exception of silver and iodine, the interference by the elements increased rapidly with atomic number. The apparent uranium content of 1% solution of 22 ions varied from less than 0.1, in the case of the acetate ion, to 9.6 g of uranium per liter in the case of thorium. Moderate concentrations of substances of low atomic numbers such as sodium, amonium and fluoride ions, did not even interfere, but chemical separation of the uranium was necessary when appreciable quantities of many other elements were present.

He used by this method the polychromatic radiation from a tungsten target tube, and the transmitted intensities of the two portions of the X-ray beam were matched by adjusting an aluminium wedge-type attenator disk, in one portion of the beam until the absorption by the aluminium was equivalent to the absorption by the sample in the other portion of the beam.

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3.2 — Absorption-fluorescence technique

This method, is mainly used for the determination of thicknesses. In this method the poly-chromatic beam excites the characteristic lines of the substrate after the beam has gone to the film or cladding. A constant fraction of the quanta thus excited will leave the sample on the side from which the plychromatic beam externs. So doing, these quanta will have to penetrate for instance the film resting upon the substrate and they will be absorbed to an extent that depends upon the thickness of the film.

The attenuation of the X-rays leaving the substrate can therefore be used to determine the thickness of the film.

Applications

Keating and Kammerer ([28]) measured the thickness of a zirconium-nitrite film on zir-conium, by observing the attention of copper $K \alpha$ and of chromium $K \alpha$ as each passed through the film twice in its path from the source.

But a recent and more important determination being carried out, is that of cladding thickness of nuclear fuel elements, because this absorption-fluorescence technique is an accurate, rapid and non-destructive method to determine this cladding thickness. This technique is also very sensitive in the appropriate range because the attenuation of X-rays in a linear direction through any material is an exponential function of the thickness of the absorber and secondly, the attenuation of a particular wavelength is a function of thickness only, and is not affected by small amounts of impurities, heat treatment or other previous metallurgical preparation.

M. Lambert ([29]), measured thickness of 11 W/o and 14 W/o plutonium-aluminium and enriched uranium-aluminium cores in reactor fuel plates by this method in the range of 0.001 to 0.030 inch, with a sensitivity of $\pm$ 0.00025 inch by using the uranium L B$_1$ line.

P. Lublin ([30]), determinated zirconium clad fuel pins in the 0-3 mil range, using the atten-uation of the uranium $L \alpha$ line. The accuracy depended on the analysis desired.

Lowe, Sierer and Ogilvie ([31]), measured thicknesses of zirconium up to 30 mils using the uranium $K \alpha$ line, with an accuracy of 3%, by using a 150 KV X-ray source.

Aluminium cladding to 30 mils thickness with an accuracy of 1% and stainless steel cladding in the range from 0-10 mils were also measured. For stainless steel cladding thickness greater than 10 mils it was possible to measure Compton scattering from a 150 KV X-ray source, using non-dispersive analysis.

4 — ABSORPTIOMETRY WITH MONOCHROMATIC BEAMS

Polychromatic beams are intense, complex but require little equipment if they are to be used in absorptiometry.

Monochromatic beams are *weak*, simple and demand more equipment. With these beams, generally there is no need to worry about an effective wavelength, about filtration of the beam or about difficulties resulting from the presence of absorption edges. There are four kinds of mono-chromatic beams :

   a) those produced by Bragg reflection

   b) filtered beams

   c) beams in which characteristic lines predominate over a background that can be neglected

d) X-rays produced by radioactive sources. Especially the latter promises to grow in importance. But the number of radioactive sources that meet the requirements of a monochromatic X-ray source is not large. These requirements are :

a) proper half-life

b) ready availability at reasonable cost

c) suitable energy of radiation, high enough to excite fluorescence in the desired material, but not so high that its efficiency is poor and shielding a problem and

d) high specific activity.

The most promising sources for X-ray analysis are beta-ray excited X-ray sources. Some of them are : ^{90}Sr, ^{90}Y, ^{240}Tl, ^{85}Kr, ^{147}Pm, ^{32}P, ^{3}H. Potential applications for bremstrahlung, beta and gamma excited X-ray source may include : radiography, thickness gauging and analysis through density measurements in gas-liquid mixtures, chemical analysis by absorption using the fluorescent source as well as straight-forward fluorescence analysis using the white spectra, which may be simply obtained.

The relative small size, stability and zero power consumption may eventually make this device useful, particularly in the field where power is not available;

As further mentioned, absorptiometry with monochromatic beams can be subdivided into :

4.1 — Simple absorptiometry

This method is preferably done at a wavelength just below an absorption edge, where the absorption coefficient is high. The method is analogous to spectrophotometry at one wavelength in the ultraviolet, the visible or the infrared.

Applications

There are several applications of simple absorptiometry ([32, 33, 34, 35, 36]), but not all are specific to the field of nuclear chemistry. An original application however, which should be mentioned, is the development of the determination of the composition of multi-component alloys. When two metals are allowed to diffuse into another, a diffusion zone is formed, the shape of which is determinated by the relative diffusivities of the two elements, the time and temperature of the diffusion and the number of phases existing in equilibrium at the diffusion temperature.

This absorption technique is well suited to the analysis of such concentration gradients. It is particularly useful, where the high temperature cannot be retained at room temperature, which is necessary for the parametric phase method.

R. E. Ogilvie ([37]) for instance studied the iron-chromium and nickel-chromium diffusion couples and P. Lublin ([38]) the aluminium-nickel diffusion couple with excellent results.

4.2 — Modified differential absorptiometry

It is possible to use absorptiometry across an absorption edge, at two wavelengths that inclose but do not locate an absorption edge. This procedure resembles simple absorptiometry at more than one wavelength and it also resembles the absorption edge method. But in general this method does not seem to be very interesting.

4.3 — Absorption-edge method

If the mass absorption coefficient of an element is determinated as a function of wavelength, sharp discontinuities are observed at X-ray wavelengths characteristic of the element. These discontinuities are well-known as absorption limits or absorption edges.

In X-ray absorption edge analysis the transmitted intensities for two X-ray energies located on each side of a suitable absorption edge of the element being determinated are related to the concentration of that element.

The concept of the absorption edge technique was first applied to quantitative analysis by Glocker and Frohnmayer [39] in 1925 but only few practical applications were made during the next two decades.

X-ray absorption edge spectrometry possesses the great advantage of little or no matrix effect and is also more precise for higher concentrations than X-ray fluorescence.

At present, with a tube voltage of 50 KV, europium or gadolinium would be the highest atomic number determinable at its K-edge. For the higher atomic number elements however the L-absorption edges can be used.

Applications :

Dodd C. G. [40] has strengthened the absorption-edge method by using pulse height selection, in connection with it.

The problem was to make intensity measurements on either side of an absorption-edge so that the present amount of an element can be deduced from the magnitude of the jump in the sample at the edge. He found that the pulse height selection by means of a very thin (0.1 volt wide) window gives differential curves narrow enough so that simple measurement of differences in the peak heights of these leads directly to the present amount of the element sought.

Cauchois and Mc Taggart [41] have applied the absorption-edge method to the zirconium-hafnium system. Several possibilities were explored but no detailed results are given. Most of the work seems to have been done on the determination of zirconium. A large range of zirconium contents (ranging down to 1 mg per square inch, in a cell several centimeters long) was covered and results precise to several percent were obtained.

Dietrich and Barringer [42] used this method for the determination of molybdenum-uranium alloys in the range of 2-5% molybdenum. The uranium however had to be removed by a tributyl-phosphate extraction, because its high absorbance made the method insensitive.

The molybdenum could be determinated, with a standard deviation of 1.35% and the X-ray method was superior to that using α-benzoinoxime.

Wright and Barringer [43] measured uranium in the range of 0.001 g uranium per gram till 0.12 g uranium per gram, with a 1% deviation between duplicate samples for concentrations above 0.01 g U/g and 2% deviation for concentrations between 0.01 g U/g and 0.001 g U/g. They used a tungsten target, obtaining monochromatic X-rays by diffraction from the (100) planes of a rock salt crystal.

Stewart [44], determinated thorium, using the Th L_{III} absorption edge, directly in liquid samples containing percentage qualities of impurity elements in concentration range of 100-1500 mg of thorium per ml. Solid samples could be analyzed after dissolution. Lead and uranium in concentrations of 5000 mg per ml did not interfere. However bismuth and strontium did and to eliminate these interferences he used a butyl-phosphate liquid-liquid extraction of the thorium.

The limit of error for a single analysis at the 95% confidence level is $\pm$ 2.8% for 2000 mg of thorium per ml of solution.

Lambert [45], used the X-ray absorption edge procedure, for the determination of uranium in the concentration range between 0.5 and 40 mg per ml. In this procedure a molybdenum-niobium target was bombarded by the radiation from a tungsten target X-ray tube and the intensities of the fluorescent X-rays of the molybdenum and niobium are measured after they have passed through an absorption-cell filled with the sample solution.

The relative standard deviation for the concentration range of 0.5-40 mg of uranium per ml varied from 6-0.34%.

This procedure could also be applied to the determination of yttrium.

R. E. Barringer ([46]) determinated uranium directly in concentrations of 0.5-0.02 gram per ml. Higher uranium concentrations could be analyzed by dilution, while solid samples were dissolved to be analyzed in the same manner.

By using the L_{III} absorption edge of uranium at 0.72 Å, he found that three elements interfere with the analysis, namely yttrium, polonium and possible radon, but all other elements from strontium, through the lower atomic numbers did not interfere.

Finally Dunn H. W. ([47]) has determinated zirconium in pure Zr-solutions and Zr-solutions contaminated with stainless steel, ytttrium, uranium and aluminium. These elements selected as impurities were chosen because they have absorption edges near the Zr-K absorption edge and were the most likely elements to cause trouble. But the results showed that the impurities evidently caused little or no interferences.

As precision he found for Zr a relative standard deviation of 1 percent for concentrations down to 1 mg/ml, 3 percent for 0.2 mg/ml and 50 percent for 0.05 mg/ml.

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