USE OF X-RAY FLUORESCENCE SPECTROMETRY TO DETERMINE TRACE ELEMENTS IN GRAPHITE

by

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Abstract

This paper deals with application of X-ray fluorescence spectrometry for the detection of trace elements in graphic. An X-ray spectrometer was constructed and used to carry out measurements on graphite spheres impregnated with different chemical elements. The intensities of the K_α lines of these trace elements, as function of concentration, were measured in order to establish the sensitivity of the spectrometer. These measurements have shown that X-ray fluorescence methods can easily be employed for detection of trace elements in graphite samples with conventional X-ray tubes, the sensitivity of the spectrometer was about 29 ppm for Zr

INTRODUCTON

Graphite is a material which finds important applications in nuclear technology. It is used as a moderator in nuclear reactors and cladding material for reactor fuel elements (Hecker et at 19(7)).

In these applications, very high purity is required of graphite. Impurity atoms, especially those with large neutron absorption cross-sections must be kept down to concentrations of a few parts per million. In the work reported here, an X-ray spectrometer was constructed and used to detect the presence of trace elements in graphite matrix by their K fluorescence X-ray lines.

Equipment

The spectrometer consisted of an X-ray tube (as primary source), a sample holder and a turn-table carrying the analyzer crystal and the detector, all mounted on an optical, bench. Collimation of the X-rays was achieved by means of soller slits placed between sample and crystal, and between crystal and detector. The detector output was connected to electronic readout instruments. To provide biological shielding, both the X-ray tube and the sample were surrounded by 5 cm-thick lead walls and covered from above with a 6 mm-thick lead sheet. Figure 1 shows schematically the experimental arrangement.

The X-ray tube employed was a Phillips 2Kw tube with molybdenum target. A 100-kv generator supplied the required high voltage. The turn-table consisted of two pairs of worm and worm-wheel segments rotating about a common axle. The larger segment carried the detector while the analyzer crystal was mounted on the smaller one. Driven by a common shaft, the detector rotated at twice the angular speed of the crystal - a requirement that ensures that X-ray diffracted from the crystal always entered the detector. Each pair of worm and worm-wheel segment could be un-coupled and separately adjusted by means of a rotating barrel provided with a scale for reading angles. The sample holder was constructed in such a way that the position of the sample could be adjusted independently in three mutually perpendicular (x,y,z) directions. For the diffraction of the fluorescence X-rays, a large single crystal of germanium with a number of deep grooves, each 2.1 mm wide, cut into it, was used. The walls of the grooves, which were cut parallel to the 220-crystal plane, formed pairs of analyzer crystal. This form of the crystal had the following advantages:

(i) for small crystal lengths, and the X-rays coming from the source collimator were encompassed by the crystal even for small Bragg angles;

(ii) with suitable length of the crystal, multiple Bragg reflection of the incident X-rays was achieved (Bonse and Hart, 1965). This improved the signal/noise ratio and led to better resolution.

The diffracted X-rays were detected with a NaI(TL) scintillation counter - photomultiplier from Hanshaw Chemical Company. In the wavelength interval (0.34A - 0.8A) considered here, this detector has high quantum efficiency and high counting rate (up to 10^5 sec^{-l}) without significant dead time losses. For measuring and plotting the fluorescence intensity, a ratemeter, a single-channel analyzer and a chart-recorder were used.

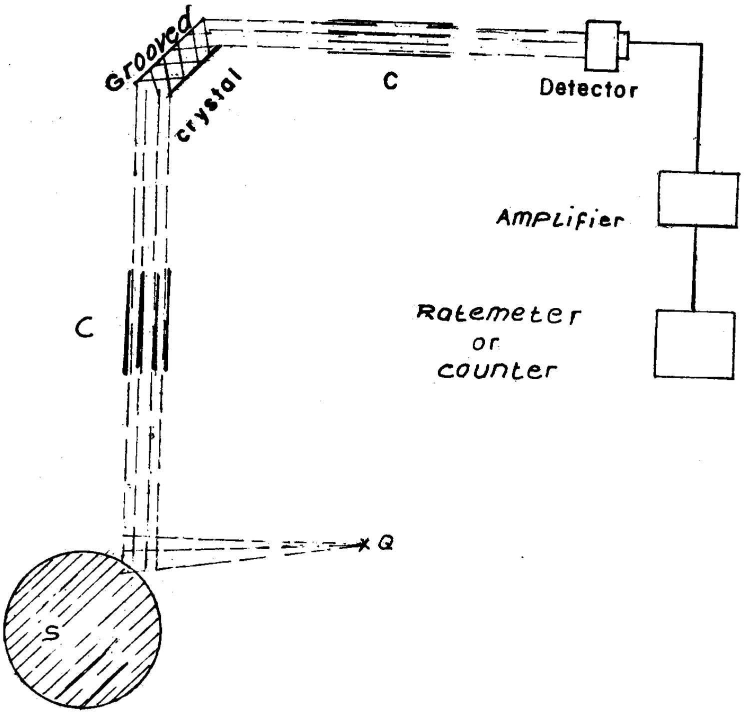

Figure 1: Schematic diagram of the experimental set-up

Samples and Sample Preparation

The samples used in the experiment were spherical graphite shells 6cm in diameter and 1.2 cm thick, the type used in the manufacture of pepple-bed reactor fuel elements (Schulten and Hecker, 1968). These were impregnated with, various chemical elements. A water solution of the nitrate or chloride of the selected element was pressed into the open pores of the graphite shell under a pressure of 250 atmospheres in an Austenite pressure chamber (for ca 30 min.). On removal from the chamber, the sample was left for some time in the solution for dimensioning. Thereafter, the graphite sphere was wiped with absorbent paper and weighed. From the difference in weight before and after impregnation the concentration of the element in the graphite was determined. The samples were then dried and annealed in a muffle oven which could be heated to a temperature of 1100°C. Along the entire length of the oven was a central steel tube with an inner diameter greater than 60mm, whose ends rested on ball-bearings.

This tube, which contained the samples, was driven by an electric motor via a pulley and an eccentric disc - an arrangement which made possible the simultaneous rotation of the tube about its longitudinal axis and a tilt movement of the entire oven about a lateral axis. In this way, the graphite spheres in the oven moved about two mutually perpendicular axes, thus ensuring uniform distribution of the trace .elements in the samples. The steel tube was sealed at one end with a blind flange and connected at the end to a vacuum pump system by means of gasket. The equilibrium pressure in the tube during heating was about 10^{-1} torr. The temperature of the oven and the tube were measured with thermo-elements. During annealing of the graphite spheres, the nitrates and other compounds of the impregnating elements changed into their oxides. Samples with Y, Zr, and La in concentrations between 10 and 400 ppm were prepared as described above. Table 1 gives the energy, the wavelengths and bragg angles of the K_α lines of the trace elements.

Table 1. Trace elements and their lines

Element	Line	Energy(kev)	Wavelength(A°)	Bragg angle, 20 (220 – Reflection)
La	K_1	33.44	0.3753	10.42°
La	K_2	33.03	0.3707	10.68°
Y	K_1	14.95	0.8330	24.51°
Y	K_2	14.88	0.8288	24.48°
Zr	K_1	15.78	0.7901	23.27°
Zr	K_2	15.69	0.7859	23.14°

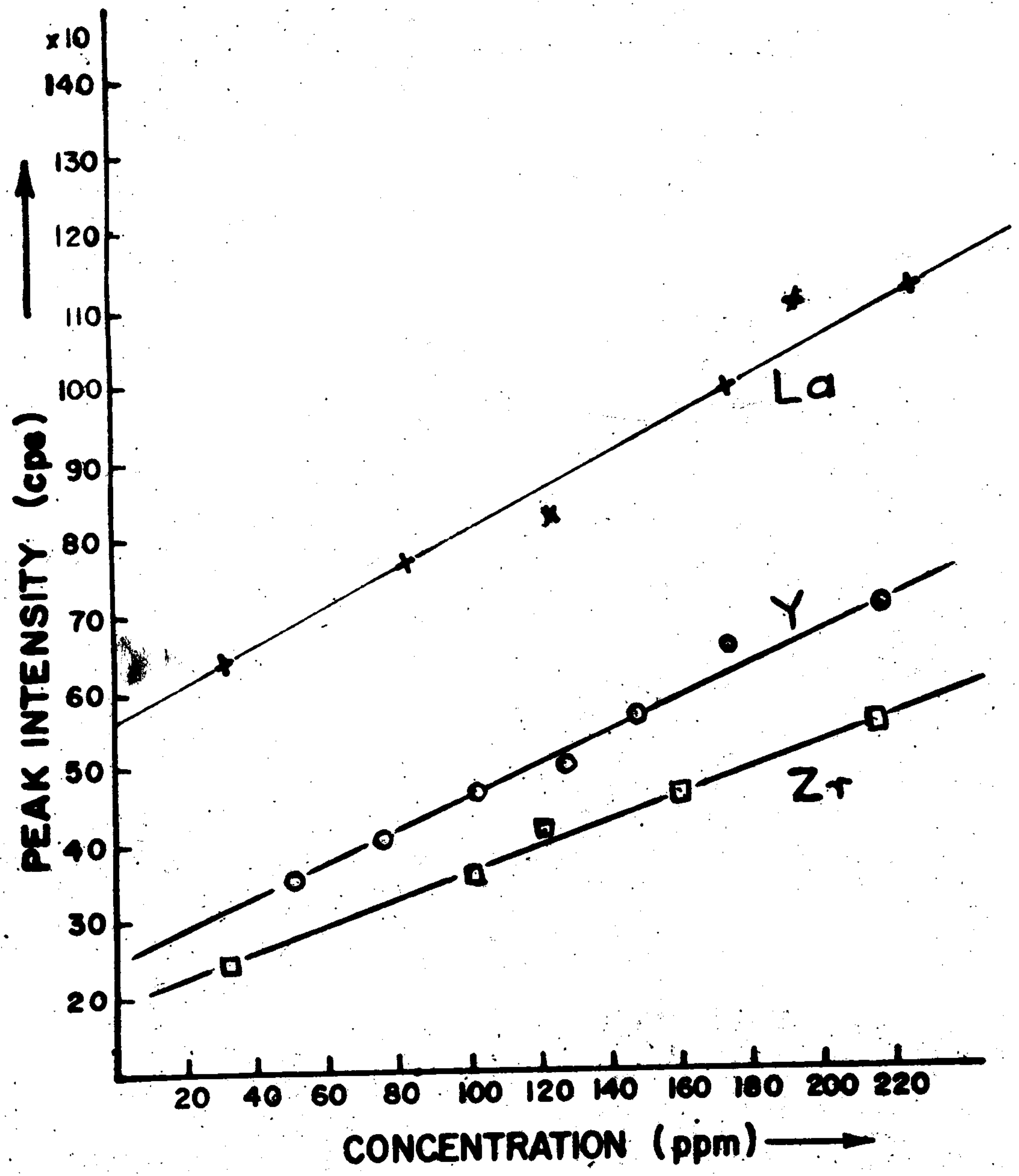

Figure 2: Graph of the intensity of Kα line as function of concentration for samples containing zirconium, yttrium and lanthanium

Procedure

After the spectrometer had been set up, the position of the sample holder, and the values of tube voltage and current were adjusted to give the maximum excitation of fluorescence radiation. The intensity of K_α-lines of the trace elements were then measured after reflection from the (220) plane of the Ge crystal - the detector voltage, the discriminator and other electronic controls having been selected for the best signal/noise ratio.

The trace elements together with their, K-excitation potential, the wavelengths of their K_α lines and the Bragg angles for the 220-reflection are given in Table 1.

Results

Figure 2 shows the results of measurements on three groups of samples. The samples in each group contain the same element at various concentrations, and measurements were carried out with identical settings of the instruments. The results are presented as graphs of K_α fluorescence intensity vs concentration. The intensities plotted are the peak intensities of the fluorescence K_α lines. For each measurement; the diffracting crystal was set at the exact Bragg angle, corresponding to the peak of the intensity curve as monitored by the trace of the chart-recorder. The number of counts per second at this position was recorded by means of the timer and scaler.

Discussion of the Results

As can be seen from the graphs, the plot of the peak intensity vs concentration is a straight line having intercept on the intensity axis. The intercept represents the intensity at zero concentration of the impregnating element, or the background intensity. Knowing the background intensity I_B, the sensitivity of the of spectrometer employed could be determined. Sensitivity may be defined as the minimum concentration of a trace element which can still be determined with certainty under given experimental conditions.

Quantitatively, it is defined as that concentration which would give a peak intensity higher by $3\sqrt{I_B}$ than the background intensity I_B. From the graphs in figure 2, the background intensities for the various groups of samples are obtained.

Using the definition of sensitivity, it can be determined that, under the conditions of the experiment, trace amounts of Y(68 ppm), Zr (30 ppm), and La (39 ppm) in graphite can be detected with certainty.

Conclusion

With conventional X-ray tubes, the K_α-lines of all the trace elements investigated could be detected at concentrations down to about 30 ppm. In most cases, trace element concentrations of this order will be tolerable in applications of graphite.

References

1. Hecker R., Rausch W. & Schulten R. (1967) Development of High Temperature Thermal Reactors in Germany EU R 3493
2. Bonse U. & Hart M. (1965) A new tool for small-angle X-ray scattering and X-ray spectroscopy: The multiple reflection diffractometer, Appl. Phys. Letters, 7, 238 (1966)
3. Schulten R. & Hecker R. (1968) Atomreakto mit Brennstoffkugeln. Umschau der Wissenschaft and Technik, 7, (1968)
4. Bertin E.P. Principles and Practice of X-ray Spectrometric Analysis. Plenum Press, New York, London (1970).