A Commercial Spectrometer Modified for X-ray Spectroscopy of the Light Elements

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29434

Abstract. A description is given of the simple modifications required to adapt a Norelco vacuum x-ray spectrometer for light element analysis. Data are given showing its spectral efficiency for wave lengths through the $K\alpha$ line of boron ($\lambda = 67A$).

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Conventional x-ray spectroscopy has been highly successful in the analysis of elements heavier than silicon and has given results of limited accuracy and sensitivity for aluminum and magnesium. It has failed for lighter elements because of the low efficiency of the fluorescent excitation of their characteristic x-rays and because their very long wave lengths could not be analyzed in spectrometers built to deal with the harder radiations from heavier elements. Recent developments in ways to excite very soft x-rays and in techniques for their measurement now make it relatively easy to analyze for the lighter elements through boron [$\lambda(K\alpha) = 67A$]. We are describing here a simple modification of a commercial x-ray spectrometer which permits this extension.

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The problem of low x-ray production by light elements can be met (1,2) by eliminating the window between the tube target and a "fluorescing" sample this will increase by as much as one thousand fold the output of characteristic x-rays. Single crystals are not available with spacings great enough to reflect the x-rays from elements lighter than oxygen but stacked monomolecular films of lead stearate or other fatty acid salts will act as very efficient gratings with 2d spacings at least as large as 125A. The counter tubes ordinarily employed will not record the x-rays in question because of absorption in their windows but they are satisfactory when equipped with stretched polypropylene or even with thin collodion windows.

After having carried through extensive measurements with a spectrometer especially arranged for the study of long x-rays, we have applied the x-ray source, grating and detector developed for this instrument to the commercially available Norelco vacuum spectrometer to see how it would perform in this extension of x-ray spectroscopy. The gas type x-ray tube, (B in Figure 1) mounted in this Norelco spectrometer, is an obvious modification of that recently described (1); it is built around a casting for a standard FA-60 x-ray tube and fits as a direct replacement for such a tube. The target, which is exchangeable, is water cooled through the same leads that cool an FA-60. The power consumption of the gas tube for this work is so small (about 25 watts) that no other water cooling is required. The

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sample is placed in one of the usual specimen holders from which the mylar has been removed and there is no window between it and the anode of the tube. For work with soft x-rays it is important that low voltages be used to minimize background due to white radiation. The standard, unmodified Philips power supply, operated at its lowest value between 10 and 15 KV, can be employed for the analysis of elements heavier than fluorine but for this element and those still lighter better results are obtained if the tube is operated in the region from 5 to 10 KV. In view of the small power needed - in none of our experiments with this instrument has it exceeded 100 watts - an inexpensive power supply has been adequate. The tube operates at a vacuum of about 20 micra and no difficulty has been experienced in creating a better vacuum than this throughout the apparatus with the Welch #1402 oil pump that routinely evacuates the spectrometer. For quantitative measurements of intensity it is obviously essential to have a constant x-ray output. This is readily obtainable by introducing a controlled air leak into the pumping system. It can be done with such a precision needle valve as the Whitey 22RS4-316(3) connected directly to the atmosphere but we find it somewhat better to connect the valve to a buffer tank (an old butane bottle, for example) which is partially evacuated every day or two.

As an analyzing "crystal" a 130-layer (4) lead stearate (LS) grating is commonly employed. Such a "grating" is not difficult to prepare with a modified Langmuir trough. Analyses with greatly increased sensitivity can now be made for silicon and aluminum with an ethelyene diamine tartrate (EDT) crystal and for lighter elements with mica or potassium acid phthalate (KAP) crystals. If the stearate grating is to be used to measure the heavier of these light elements, this should be done in a higher order to avoid the high background at low angles of reflection. An idea of the relative efficiencies of the three crystals and the stearate grating can be gained from the fact that the intensities of the first order Kα lines of aluminum are in the ratio 100 (EDT) : 27 (mica) : 70 (KAP) : 200 (LS). Intensities of the several orders of a spectral line from a typical LS grating are in the approximate ratio 100 : 19 : 12 : 3 : 2 for its first five orders. As we make them such a grating is built up on a 1"x3" microscope slide which can very simply replace the second crystal in the double crystal holder of the Norelco spectrometer.

The flow proportional counter of the commercial instrument can be used as detector for the long wave lengths with only a change of window. This window is, however, so large that it is customary to coat its inner surface with aluminum or carbon for stable operation. Such a coating increases unnecessarily the opacity of the stretched polypropylene; it can be avoided by facing the new window on the counter side with aluminum foil cut to cover all but an area of about 7x25 mm of the Soller slit. The P-10 counter gas conventionally employed in x-ray spectroscopy will record long x-rays;

and the higher counter voltages required, up to about 1900V, are within the range of the circuit panel customarily employed with this instrument.

Figure 2 shows typical spectra obtained with the Norelco spectrometer as modified above; backgrounds are low and peak-to-background ratios satisfactory; Table I gives the observed efficiencies of $K\alpha$ lines (in counts per second per watt of energy through the x-ray tube) measured for several elements. Numbers in parentheses are observed values adjusted for 100% content of the element but not for absorption. They have no absolute significance and depend on many factors including a tube voltage which will ordinarily be chosen to give the optimal peak-to-background ratio for the elements being analyzed. The intensities shown in the figure can easily be increased by raising the power through the tube, but they are sufficient to permit accurate analyses for small amounts of all the light elements except nitrogen. The low efficiency for nitrogen recorded in the table is due to the extreme absorption of its characteristic x-rays by the carbon of the counter window; this is a situation that will always prevail unless a suitable noncarbonaceous window material is found.

Table 1. Observed Peak Heights (in c/s/w) of LS Spectra of Light Elements

Element	Spectral Order	
	1st	2nd
Aluminum	—	400
Magnesium	—	394
Sodium (NaCl)	—	(292)
Fluorine (LiF)	(840)	(203)
Oxygen	(196)	(28)
Nitrogen	(13)	—
Carbon	1100	—
Boron	(480)	—

References and Notes

(1) R.W.G. Wyckoff and F.D. Davidson, Rev. Sci. Instr. 34, 572 (1963).

(2) R.W.G. Wyckoff and F.D. Davidson, Rev. Sci. Instr. 35, 381 (1964).

(3) Purchased from Whitey Research Tool Co., 5525 Marshall St., Oakland 8, Calif.

(4) R.P. Frans and F.D. Davidson, Rev. Sci. Instr., in press.

(5) This work has been supported by National Aeronautics and Space Administration Grant NsG-120, National Science Foundation Grant GB 1322 and National Institutes of Health Grant DE 01919.

Legends for Figures

Fig. 1. A photograph of the Norelco vacuum spectrometer arranged for soft x-ray measurements. The gas type x-ray tube is at B and the vacuum leak at A.

Fig. 2. The Kα lines of boron, carbon and oxygen as recorded with the spectrometer of Fig. 1. All spectra were taken with 25 watts through the tube. For carbon the sample was compressed graphite. The spectra for boron and oxygen at the right were obtained from pressed boric acid.

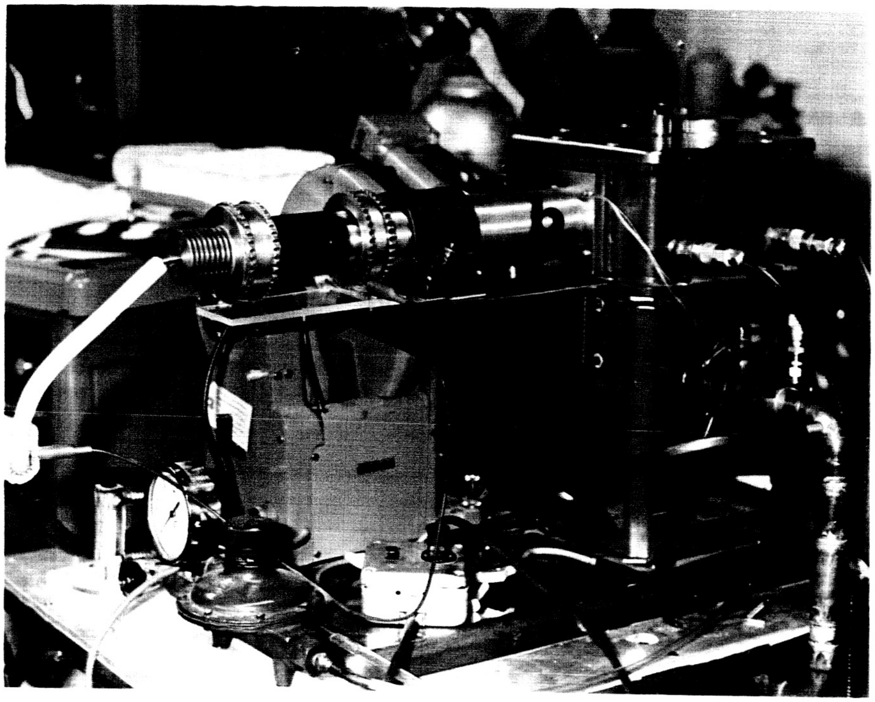

Fig. 1

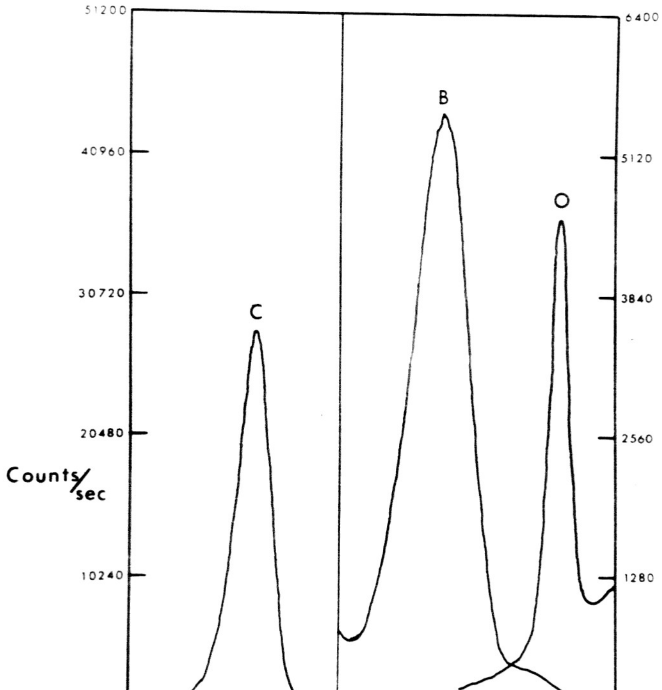
51200
40960
30720
20480
10240
6400
5120
3840
2560
1280
Counts/sec
C
B
O
60
56
54
48
92
36
88
32
84
28
80
24
Angle

Fig. 2