

## NOTES AND NEWS

### NOTES ON THE RELIABILITY OF THE X-RAY DIFFRACTION SPECTROMETER FOR QUANTITATIVE MINERAL ANALYSIS\*

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The use of the Geiger-counter  $x$ -ray diffraction spectrometer for mineral identification and analysis is becoming more widespread as the convenience and reliability of this equipment are appreciated by more workers in the field. There is, consequently, increased interest in specific techniques employed when this instrument is used for quantitative mineral analysis.

A recent paper (1) by this author, discussing certain aspects of quantitative  $x$ -ray analysis and presenting a specific technique employing a Geiger-counter spectrometer for mineral-powder analysis, has been subject to a criticism (2), which appears quite unjustified in the light of the experience of the writer.

One point of this criticism was that by this technique, "considerable amounts of *colloidal* quartz, if mixed with other well-crystallized materials, could be present and yet elude measurement, especially if well-crystallized quartz were also to be found in the mixture." In all fairness to any method of  $x$ -ray diffraction analysis, it must be admitted that no technique developed for well-crystallized mineral powders would have much value in working with either colloidal or amorphous materials. Such limitations are certainly universally recognized.

Secondly, it was not intended to be implied that "variations in the  $x$ -ray output are more serious in the case of the photographic method than in that of the Geiger-counter spectrometer," as charged by Dr. Lonsdale. It was merely pointed out that, for short exposures, variations in total  $x$ -ray output may be *significant* when only one measurement per analysis (a film density), is made.

The main part of Dr. Lonsdale's criticism was devoted to an expression of disbelief in the linearity of response of the automatic recording spectrometer, except "over a very restricted portion of the graph" and a consequent limited usefulness for quantitative analysis was therefore inferred. It was also pointed out that, "The instrument ceased to record, even at highest sensitivity, at an intensity which was certainly more than 100 times the minimum intensity observable with a scaling circuit and mechanical impulse counter."

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The technique described in the original paper is such that good linearity of response, or the lack thereof, is immaterial to the successful performance of quantitative analysis. A complete calibration of the equipment is obtained by determining standard working curves which incorporate in their development the characteristic response of all the

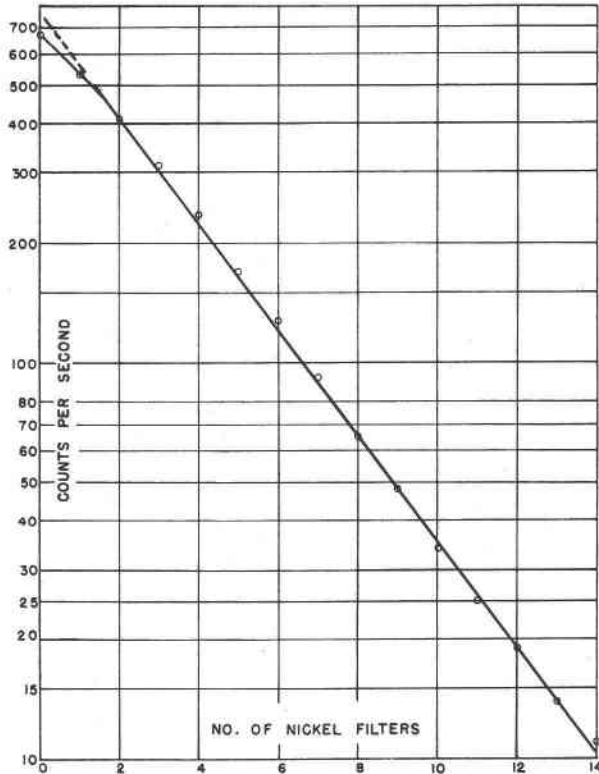


FIG. 1

elements of the apparatus. The only assumption necessary is that these responses remain constant during an analysis and can be standardized and hence reproduced from day to day. The sensitivity of the recording method is sufficient to obtain accurate data on as little as 1 to 5 per cent of a material, on about 2 per cent of quartz. Of course, scaling and mechanical counting would extend this lower limit to smaller values but at a sacrifice to the speed of analysis. Likewise the actual linearity of response of the equipment is excellent over most of the range of counting rate used. The following graphs illustrate this point.

Figure 1 presents a plot of counts per second, on a logarithmic scale, versus number of filters (nickel foil) superimposed in the diffracted beam. It indicates that, for rates between 10 and somewhat above 400 counts per second, the linearity of the Geiger-tube response is good. Figure 2 shows the excellent linearity of the recorder unit from 5 to 100 (full-scale) divisions. Inquiries to other investigators have revealed that this type of performance is typical of many x-ray diffraction spectrometer installations and is not an exceptional one.

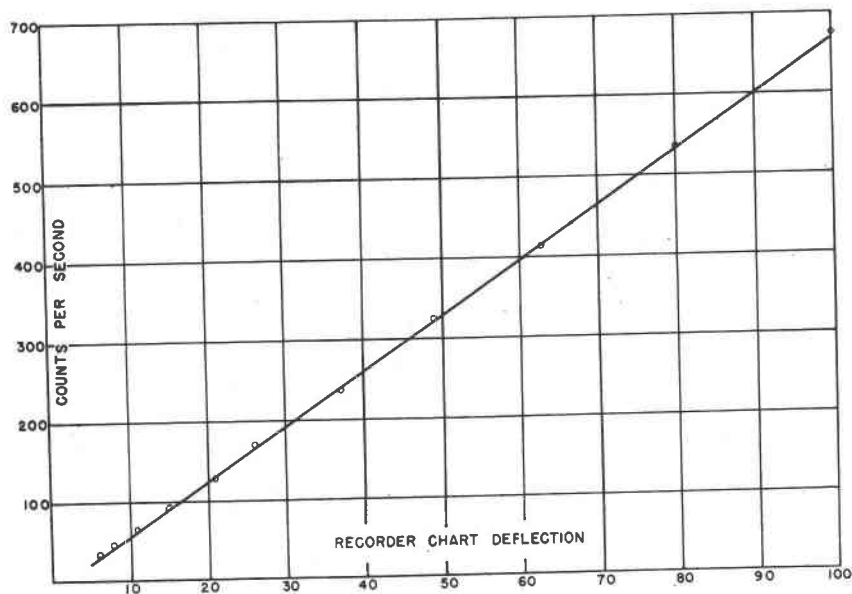


FIG. 2

Further work with this equipment has shown that the standard conditions under which the working curves were originally obtained are not so critical that changes, renewals, or readjustments in the component parts of the equipment will invalidate these curves to the extent of necessitating their complete redetermination. Within the limits of accuracy of analysis originally stated, plus or minus 10 per cent of the amount present, after such changes a readjustment of the coupling control sensitivity to give the original deflection for one or more of the standard samples, including the 100 per cent sample, has been found sufficient to reproduce satisfactorily the original working curves. That is, the installation of a new Geiger-counter tube, new electronic tubes, and a complete realignment of the spectrometer produced no material distortion

in these working curves. This indicates that the characteristic responses of the equipment were not appreciably altered by such changes.

Although there is theoretical evidence that scanning at a slower rate than, say, 1 R.P.M., should produce more reliable values of recorded intensities, in practice no significant difference has been observed between scanning rates of  $\frac{1}{2}$  R.P.M. and 1 R.P.M. in the reproducibility of results. In other words, a slower scanning rate itself does not allow a reduction in either the number of intensity recordings on the same sample or in the number of sample mounts necessary. However, for many analyses, particularly those in which the concentration of the mineral is above 10 per cent or so, very satisfactory results have been obtained at the 1 R.P.M. rate with only three determinations of line height on three different mounts, instead of the usual five. The time for an analysis is reduced thereby from about 45 to about 30 minutes. On the other hand, with proper care at all stages of the technique, results good to about plus or minus 5 per cent of the amount present, when the mineral concentration was above 10 per cent, have been achieved on "ideal" samples. Such "ideal" samples are those having strong and isolated diffraction lines, no preferred orientations, and forming readily reproduced mounted surfaces.

#### REFERENCES

1. CARL, HOWARD F., Quantitative mineral analysis with a recording  $x$ -ray diffraction spectrometer: *Am. Mineral.*, **32**, 508-517 (1947).
2. LONSDALE, KATHLEEN, Note on quantitative analysis by  $x$ -ray diffraction methods: *Am. Mineral.*, **33**, 90-92 (1948).

#### A NEW OCCURRENCE OF HELVITE\*

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Helvite has been found in a zinc replacement deposit in limestone at the Grandview mine in the Black Range, Grant County, New Mexico. So far as is known, this mineral has not previously been found in a deposit of this type. The various types of occurrence and associations and the properties of helvite and the helvite group are described in a paper by Glass, Jahns, and Stevens.<sup>1</sup>

While mapping one of the replacement zinc deposits in limestone at the Grandview mine in the Swartz district, Grant County, New Mexico, the author collected a specimen of fluorite from a vug in the ore body. Subsequently tiny tetrahedrons of yellow helvite were discovered in the

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<sup>1</sup> Glass, J. J., Jahns, R. H., and Stevens, R. E., Helvite and danalite from New Mexico, and the helvite group: *Am. Mineral.*, **29**, 163-191 (1944).