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UNITED STATES  
DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Technical Letter  
Saudi Arabian Mineral  
Exploration - 26  
September 7, 1965

Dr. Fadil K. Kabbani  
Deputy Minister for Mineral Resources  
Directorate General for Mineral Resources  
Ministry of Petroleum and Mineral Resources  
Jiddah, Saudi Arabia

Dear Dr. Kabbani:

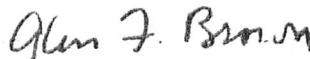
Transmitted herewith are 10 copies of:

TECHNICAL LETTER NUMBER 26  
EXPERIMENTAL ERROR IN SAMPLE  
PREPARATION AND SPECTROGRAPHIC  
ANALYSIS IN THE JIDDAH LABORATORY,  
SAUDI ARABIA

BY

Paul K. Theobald, Jr.\* and Charles E. Thompson\*

Sincerely,



Glen F. Brown, Chief  
Saudi Arabian Mineral Exploration Project

\* U. S. Geological Survey, Jiddah, Saudi Arabia

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Paul K. Theobald, Jr.\* and Charles E. Thompson\*

The histograms presented here provide a measure of the experimental error inherent in the results of spectrographic analysis during the first five months of operation by the U. S. Geological Survey in the laboratory of the Directorate General for Mineral Resources, Ministry of Petroleum and Mineral Resources in Jiddah, Saudi Arabia. Each histogram is a summary of 39 analyses of one sample for one element.

This control sample is a composite of the sediment from two adjacent, minor stream channels that head in the debris from the ancient mine at Ablah. The sediment was sieved at the sample site and only material passing through a 30 mesh sieve and remaining on an 80 mesh sieve was retained and sacked for transport to the laboratory. In the laboratory the sample was split and one half was retained in the original sack. The other half was further split in a Jones splitter to portions filling about half the volume of standard laboratory sample cartons. These splits are stored with the one half split of the original sample in the sample preparation room at the laboratory. The sample bears the field number 10-9609 but has never been submitted for analysis with this number.

Splits of this sample have been given a number in sequence with other samples in each group submitted for preparation and analysis by Theobald since collection of the control sample. There has been no system to the insertion of the control sample except that it has appeared at least once in every group of samples. It was prepared for analysis with the group without knowledge on the part of the preparator

of the samples

\* U. S. Geological Survey, Jiddah, Saudi Arabia

that it differed from other samples. It was analysed in sequence with the other samples. Thompson was aware that the control sample was in existence but did not know before analysis which samples of a group were splits of the control sample. In some groups of samples the composition of the control is sufficiently different from the rest that it could be recognized during analysis, most commonly on a basis of the lead determination. Although he may have involuntarily read the spectra for the control sample somewhat more carefully after its presence was detected, we feel that the effect of recognition of the sample has been slight because: (1) it was recognized in less than half of the determinations; and (2) there is no evidence for increased precision of those elements read after lead in comparison with those read before lead.

The spectrographic procedure is a field-type analysis based on the method followed by the Exploration Research Branch of the U. S. Geological Survey. This procedure, slightly modified to suit the equipment available, was designed for geochemical exploration purposes where rapid scanning of large numbers of samples for many elements is required. The method is a D.C. arc technique with visual comparison of unknown with standard films. Before analysis all samples are reduced to a powder in a small ceramic ball mill and a 10 milligram portion of the powder is weighed and transferred to an electrode for analysis. The following elements, with their lower limit of sensitivity in parts per million, are being determined routinely: Ag 1, B 10, Be 2, Bi 20, Cd 50, Co 5, Cr 10, Cu 10, Ga 10, Ge 20, La 20, Mn 20, Mo 2, Nb 50, Ni 5, Pb 10, Sb 200, Sc 10, Sn 10, Sr 50, Ti 10, V 20, W 50, Y 10, Zn 100, Zr 20. These limits of sensitivity may change from time to time or sample to sample, so should not be taken as an absolute value. The upper limit for all of these elements is 10,000 ppm; that is, 1 percent.

The control sample was intentionally chosen to be more metal-rich than the average, thereby affording information on a greater range of elements in a single sample. Only five of the 26 elements currently being determined on a routine basis are consistently below the limit of detection: Cd <50, Ge <20, Nb <50, Sb <200, and W <50 ppm. Two of the elements presented in the histograms, Be and Bi,

are apparently slightly below the limit of sensitivity. About half of the Bi determinations reported as 20 were questioned since the spectral line, though present, was slightly weaker than the line of the 20 ppm standard. We suspect that the Bi content of the control is 10 to 15 ppm. The median content of the other 19 elements is well within the range of the analytical technique.

The results presented in the histograms are largely self explanatory. The determinations for each element vary from time to time within a range that is about a half an order of magnitude or a little more. For some elements, like Ba, Cr and Pb, the precision appears to be somewhat better while for others, notably Sc, V and Zr, the precision is not so good. The greater part of the variation is time dependent and the precision of approximately contemporaneous determinations is considerably better than these histograms would lead one to believe.

The range of analytical results reported is a composite experimental error extending from splitting and preparation of the sample through the various steps of analysis and recording of the data. Only one typographical error was corrected in preparation of the histograms: a manganese determination was written as 100 rather than 1000 ppm. The potential for error in this sequence of events is best recognised when it is realized that the sample weighed for analysis is only 10 milligrams. A one milligram error in weight is a 10 percent discrepancy in the analysis and a microgram of contaminant adds 100 ppm to the determination. Furthermore, the time interval represented in these determinations is approximately the first five months of operation of a new machine. Several changes in techniques have occurred during the period in question and these have been accompanied by slight shifts in the results obtained for the control sample. The most conspicuous change of this type was an increase in arc temperature resulting from a change in the arc current from 9 to 12 amperes. This resulted in a slight apparent increase in the values reported for La and Ti and accounts for the bimodal distribution of the Sc, V and Zr determinations.

Changes in technique have been made somewhat more often during the initial period of operation than will be made later, but they will continue to occur

sporadically throughout the operational life of the equipment. For example: (1) the grating has been changed to facilitate rubidium determinations, (2) filters have been ordered to reduce background on the spectra and facilitate reading, and (3) a new operator will take over the machine when Thompson leaves. A shift in the apparent amount of metal can be expected from each of these changes. In order to monitor the effects of these and less conspicuous changes, we recommend that the geochemist-geologist continue to submit sample 9609 on a systematic basis.

The histograms provide the first base for interpretation of spectrographic data. Two samples that, for a given element, differ by a half an order of magnitude or less must be considered, within experimental error, to be the same. If the histogram produced from data on a series of samples has approximately the same shape and range as those produced here, the series of samples must have, within experimental error, a single metal content. In general only variations consistently greater than one half order of magnitude should be considered as significant differences. There are three situations in which interpretation of a difference may be valid when the measured range is a half order of magnitude or slightly less.

(1) When all of a series of samples have been analysed at about the same time the experimental error will be less than that given in these histograms. Evaluation of the short-range experimental error must be based on data collected concurrently with the analyses. This can usually be accomplished by considering the variation of several elements. Unless a large geographic area is involved, the majority of the elements will not exhibit more than experimental variation. These elements will provide an estimate of experimental error and the few that do exhibit greater variation can then be recognized.

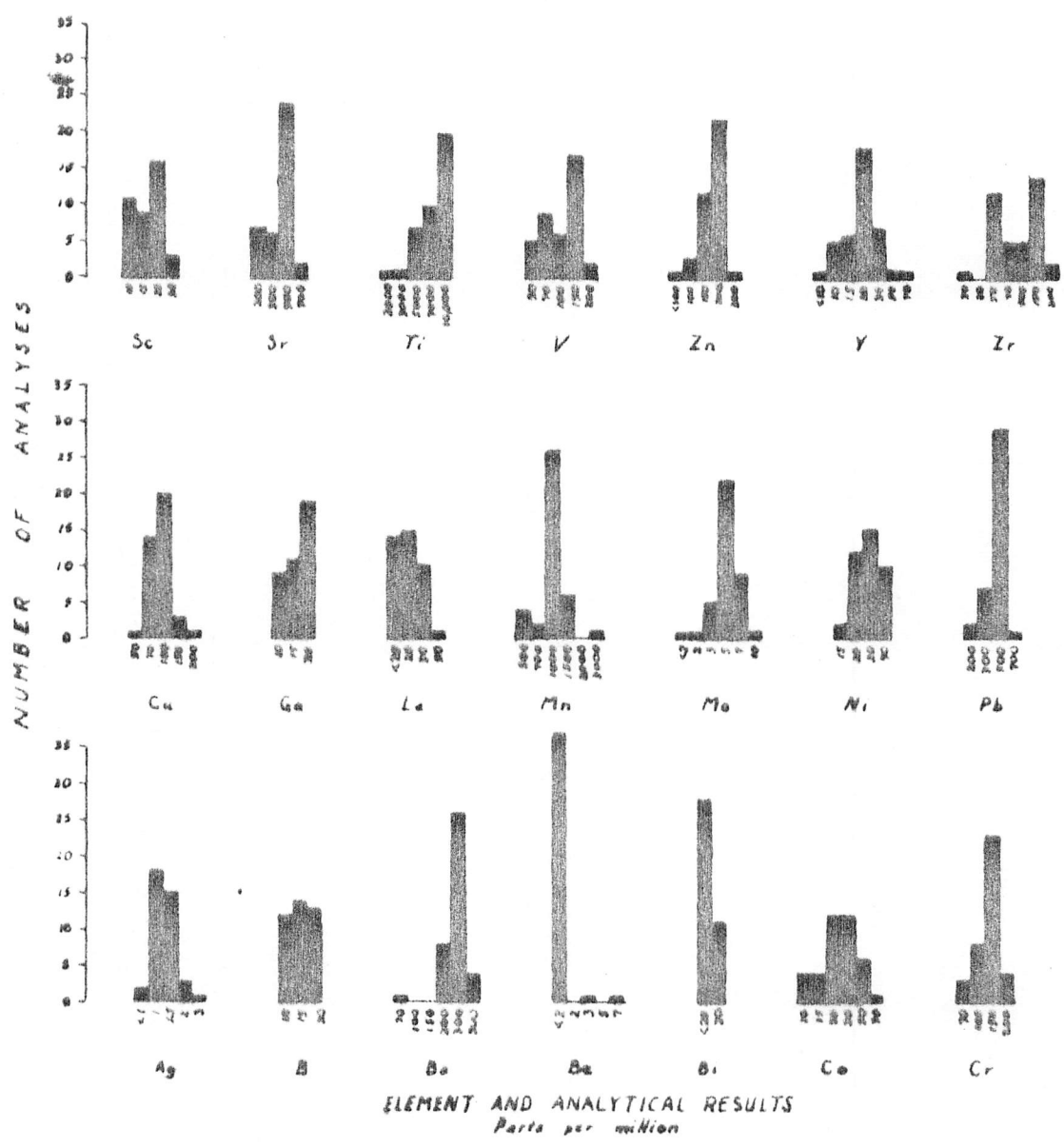
(2) When a large number of samples are involved in a study of the distribution of one element it is often possible to show that one geographic subdivision differs in composition from another even though the overall variation is not much greater than the experimental error. In this situation the mean values of the subdivisions being compared may differ by a half order of magnitude or slightly less, but because each mean is a composite of many samples it may be considered as a single,

somewhat more precise value. The validity of such comparison requires that the subdivision be independent of the sample handling procedure and that the sample handling procedure be independent of the subdivision. For example, samples collected in sequence from west to east along a line would not be subject to a geographic subdivision because the sample handling was based on geography. For example of the reverse association, a group of samples taken on a 20 foot spacing showed little variation so the interval was cut to 10 feet by collecting additional samples. Considering all these samples as a single group it was evident that alternate samples contained more of the element in question. This subdivision was not independent of sample handling, as repeating the analyses later demonstrated.

(3) When several elements exhibit parallel variation, the probability that the variation is real is enhanced. The procedure is much the same as the comparison of means described above. Particular caution must be used to ensure that the variation to be interpreted is independent of sample handling.

It is often desirable for purposes of exposition to subdivide the analytical data into sets of smaller magnitude than the experimental error even though the range for the element in question exceeds the experimental error. This procedure is acceptable so long as the expedient of exposition is not carried into a final interpretation. For example: It is commonly desirable to group analyses on a two step basis for exposition as (a) 10, 15, 20 ppm, (b) 30, 50, 70 ppm, (c) 100, 150, 200 ppm. All data of group (a) have a high probability of being different from those of group (c), but groups (b) and (c) or groups (a) and (b) cannot be considered different with much confidence. It should also be noted that the scale of measurement on the spectrograph is a geometric scale and, therefore, the grouping just given is a one half order of magnitude grouping.

The histograms presented here have a general tendency toward negative skewness; that is, more values fall below than above the mode. This probably results from the conservative nature of the analyst and his associates. Fortunately, the sample data of most value will be skewed toward higher values. Though not an absolute criterion for distinguishing natural from experimental variation, the shape of the histograms is useful in interpretation.



Results of 39 independent semiquantitative spectrographic analyses of one sample.