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THE DETERMINATION OF TOTAL VOLATILES IN ROCKS BY LOSS-ON-FUSION

By

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ABSTRACT

A fast and accurate technique has been developed for the determination of the total volatile content of rocks. The loss on fusion (LOF) results are comparable to the conventional time-consuming wet-chemical procedure but require no additional effort or cost when conducted as part of the usual sample preparation procedure for quantitative X-ray fluorescence spectrometric analysis (XRF). The technique utilizes the weight loss of the rock when fused with a suitable blend of lithium tetraborate and lithium nitrate. A simple mass balance model is used to represent the thermogravimetric results and to identify the nature of the high temperature mass alteration reactions taking place in the fusion melt. Under the sample preparation conditions used in this study, sulfide appears to be retained quantitatively in the fusion disc in the form of sulfate, a phenomenon permitting the determination of sulfide in rock samples prepared by a conventional fusion procedure.

INTRODUCTION

In the XRF analysis of a rock, the hydration water, bound water, and carbon dioxide usually are measured separately by some relatively expensive and time consuming chemical method. Most of the chemical methods for the determination of interstitial water involve the gravimetric measurement of the water driven out of a sample and collected either on filter paper (Brannock and Shapiro, 1955), in a glass tube (Maxwell, 1968), or in a U-tube containing a desiccant (Hillebrand, Lundell, Bright, and Hoffman, 1953). The organic and inorganic carbon determinations usually involve a volumetric or a chromatographic measurement of the evolved gas collected on an absorbent in a heating or fusion process (Kolthoff and Sandell, 1952; Jeffery and Kippling, 1962). Both the precision and the accuracy of the wet chemical methods depend on whether the water and the evolved CO_2 are completely recovered and measured.

In this paper, we present a simple yet heretofore neglected method for the determination of the volatile content of rock specimens submitted to our laboratory for X-ray fluorescence analysis (XRF). In contrast to the conventional wet-chemical methods which require the collection of volatiles liberated from the sample, the loss-on-fusion (LOF) method uses the weight loss of the sample when subjected to a routine fusion process (Ingamells and Suhr, 1967). Such measurements can be done accurately and routinely without significant additional effort or cost when conducted as part of the conventional sample preparation procedure for quantitative XRF analysis.

The loss-on-fusion (LOF) method reported in this note is based on the thermogravimetric accounting of reagents and products in a conventional fusion procedure for quantitative XRF analysis. In the paragraphs that follow, we

outline the analytical framework for the LOF method, some procedural details with emphasis on the blank determination, and our evaluation of the LOF method on previously analyzed rock samples. Some possible pitfalls are identified in the section on results, and additional areas for study are proposed in the conclusion.

ANALYTICAL CONSIDERATIONS

The gravimetric bookkeeping for the LOF procedure rests on the following considerations. The flux charge is prepared from a weighed mixture that includes the sample, the flux, and commonly, an oxidant and a releasing agent. In the semi-automated fusion procedure used in our laboratories, 1.0 gram of sample is mixed with 6.0 grams of lithium tetraborate flux ($Li_2B_4O_7$), 1.5 grams of lithium nitrate oxidant ($LiNO_3$) and four drops of HBr (9.0 M) releasing agent in a non-wetting 95% Pt-5% Au crucible. The mixture is fused into a glass disc by static heating for 4 minutes at $500^\circ C$ and by heating with agitation for 29 minutes at $1100^\circ C$. After cooling to room temperature, an intact fused glass disc is retrieved from the crucible and the disc weight is accurately determined. Additional details on the fusion procedure are available in an earlier report (Fabbi and Elsheimer, 1976). In general, each component of the mixture undergoes a degree of oxidation, reduction, and/or volatilization during the fusion process. In the following treatment, we evaluate the relationship between the weight of the fused disc retrieved from the crucible, the loss-on-fusion, and the gravimetric factors which reflect chemical alterations in the melt during the fusion process.

For a given flux, oxidant, and releasing agent, the fractional weight losses due to release of water, nitrogen, oxygen, bromine, etc. should be reproducible for each fusion preparation. In the mass balance equation that follows, the residual mass of the flux, oxidant, and releasing agent is represented collectively by "R," and the mass of the undried "as is" sample is designated "W." Also, "a" represents the fractional weight loss of the sample due to volatilization of constituents such as CO_2, H_2O^+, and H_2O^-, and g_N is the gravimetric factor accounting for the net mass alterations of the dry sample during fusion. The weight of the disc retrieved from the crucible will be given by:

$$D = g_N W(1-a) + R \qquad [1]$$

Solving equation [1] for the LOF term, we obtain the expression:

$$Wa = W + \frac{(R - D)}{g_N} \qquad [2]$$

The key element in the use of equation [2] for the determination of LOF is the definition and measurement of an appropriate blank. The blank must take into account the volatile content of the lithium tetraborate/lithium nitrate/bromine flux mixture, the amount of oxygen retained by the sample in the fusion process, and the amount of tightly bound water and bromine accommodated in the glass structure of the disc. The most general approach is to define the blank value, B, as the disc weight for a rock sample prepared

under standard conditions when a=0. Such a blank can be defined formally from equation [1] by setting a=0 as follows:

$$B = D_{a=0}$$
$$= g_N W + R \qquad [3]$$

A technique for the blank determination, equivalent to the above definition, calls for fusion of an accurately weighed blend of flux mixture with a rock sample for which the "a" value has been previously established by chemical methods; the relationship between the blank value and the measurable quantities can be obtained by combination of equations [1] and [3]:

$$B = D + g_N Wa \qquad [4].$$

Under general conditions in which the net gravimetric factor may assume values other than unity, the blank value as defined by equation [3] and calculated by equation [4] would be a function of the net gravimetric factor for the rock. If the net gravimetric factor is other than unity, the blank value would be unique to the particular rock under study and would lead to erroneous LOF values if used as a general characterization of the high temperature reactions taking place in the flux blend. Lack of attention to this important consideration may have precluded the success of earlier possible efforts to use the LOF measure for the determination of sample volatiles. If we are to have confidence in a direct gravimetric measurement of LOF, it will be necessary to evaluate the g_N values for a variety of rock types and generally to characterize the fusion chemistry in the sample preparation procedure.

An alternate form of equation [6] makes use of a reference rock for which the net gravimetric factor has been determined and for which the "a" value is known from chemistry determinations. In equation [7], the reference quantities are shown in italics.

$$g_N = \frac{(D-\underline{D}) + \underline{g_N}W(1-\underline{a})}{W(1-a)} \qquad [7]$$

Equations [6] and [7] were used with independently available wet chemistry volatility data to evaluate g_N values for a variety of rock samples. Figure 1, a plot of g_N values against sample index, reveals two types of behaviors. In the first type, which we will consider ideal, g_N values are close to unity indicating insignificant mass alteration during fusion. In the second type, where the fusion chemistry is less than well behaved, g_N shows considerable disparity from unity indicating measurable mass changes during fusion.

It should be noted that g_N is an operational definition; its value depends on the concentrations of constituents undergoing alteration in the melt. Accordingly, g_N values, although useful for signaling problems with the LOF determination, cannot be used for the identification of the specific high-temperature chemical reactions in the fusion melt. However, if we expand equation [1] to represent the mass alteration behavior of the complete collection of sample constituents, we obtain:

$$D = (W + R) - Wa + W\sum_i c_i(g_i-1) \qquad [8]$$

FUSION CHEMISTRY

The net gravimetric factor, g_N, is a measure of the mass alteration of the sample during the fusion process and can be used to monitor the reproducibility of the fusion chemistry from rock to rock. This factor can be understood in its simplest terms if in equation [1] we set a=0 and solve for g_N:

$$g_N = \frac{(D - R)}{W} \qquad [5]$$

Clearly, g_N is the ratio of the residual mass of the sample to the original mass of the dry sample; in the ideal fusion process, the rock component in the fusion mix will not undergo chemical alteration, and g_N will have a value of unity. The net gravimetric factor for a given rock can be easily determined from two separate fusion preparations of the same rock, each with a different dry rock weight, W and Wx. equation [1], written for the mass balance for each preparation with a=0, when solved simultaneously for g_N, yields:

$$g_N = \frac{(D_2-D_1)}{W(1-x)} \qquad [6]$$

In equation [8], the concentrations denoted c_i are expressed in terms of the "as is" sample, and the gravimetric factors, g_i, are for the ith species undergoing alteration by a particular chemical reaction. It should also be noted that the quantity (W+R) corresponds to the blank value from equation [3] for well behaved samples for which $g_N=1$. Accordingly, we can define the ideal blank, B^o, by equation [9]. The ideal blank, a property of the flux, is independent of the concentrations of species undergoing mass alteration in the melt.

$$B^o = W + R \qquad [9]$$

We now can explore the contribution of a particular chemical species to the mass alteration term of equation [8] by plotting the quantity (D+Wa) against the concentration of the species of interest. For example, if only one species dominates the mass alteration phenomenon, the simple model:

$$(D + Wa) = B^o + W(g-1)c \qquad [10]$$

will represent the concentration and disc weight data. The intercept, B^o, should approximate the theoretical value for the ideal blank, and the slope of the plot, W(g-1), can provide a qualitative clue for the identity of the chemical reaction causing alteration. If more than one species is involved, or if the species selected for study does not participate in mass alteration, equation [10] will fail to represent the data. Figures 2 and 3 show the

application of this technique with equation [10] for sulfur and for manganese, respectively. Manganese oxide was selected as a reasonable example of a species which most likely would be well behaved during lithium tetraborate fusion.

In figure 2 the curve for sulfur is strongly deterministic and linear. This linearity is a reflection of the participation of sulfur in the high-temperature chemistry. The small degree of scatter indicates that sulfur is the principal species undergoing mass alteration; all other species are well behaved in the particular set of rocks selected for examination. The intercept value in figure 2 is equal to 7.29, a number comparing favorably with the theoretical value of 7.33 (1.00g sample, 6.00g flux, and Li_2O residual due to decomposition of 1.50g $LiNO_3$). Finally, the slope of the regression line in figure 2, calculated within experimental error, is equal to 2. Hence, from equation [10]

$$g-1 = 2$$

and

$$g = 3.$$

Interestingly, a gravimetric factor of 3 is exactly that obtained for the oxidation of sulfide to sulfate (Molecular weight of SO_4/Molecular weight of sulfur).

In contrast to figure 2, the scatter of points in figure 3 indicates that some number of species other than Mn are undergoing mass alteration. If the chemistry were well behaved with respect to Mn, g_{Mn} would equal unity, the quantity (D+Wa) would equal B^0, and the curve would be linear with slope equal to zero. Note that the last four points on the right in figure 3 tend to be independent of manganese concentration and scatter around a reasonable value for B^0; as expected, manganese appears to be well behaved. The first four points on the left in figure 3, scattering substantially above the B^0 base line, revealing mass alteration not accounted for by manganese.

In summary, only one species appears to be involved in the mass alteration process for the rocks studied, vis. sulfide. The mass alteration reaction is the oxidation of sulfide to sulfate. And, under the conditions of these experiments, the oxidation is not only complete, but the sulfide originally present is also retained quantitatively in the sulfate oxidation state.

Similar excess oxidation relative to the reference blank would be expected for samples abnormally high in ferrous iron. We have detected such an oxidation pattern for ferrous iron and have made a plot similar to figure 2 for a suite of samples containing ferrous iron in the range 8-10 percent.

RESULTS

The accuracy of the LOF determination relies on the reproducibility of the physicochemical processes taking place during the fusion operation; variations in fusion conditions or fusion chemistry are reflected directly in the blank value and ultimately in the LOF value. Reproducibility and accuracy of results for the LOF measurement applied to a variety of rock types are reviewed in this section. The precision in the determination of the reference blank, B^o, is used as a measure of the reproducibility of the fusion process, and the agreement of the LOF values with conventional chemistry values for the sum of CO_2, H_2O^+, and H_2O^- provides a measure of the efficacy of equation [10].

To evaluate the reproducibility of the the quantity B^o, we used 14 international rock standards with LOF values determined by conventional chemistry. These standards, selected partly because of their negligible concentrations of sulfur, were determined to be well behaved by application of equations [6] and [7]. The blank disc weights, calculated with equation [9], have a relative standard deviation of 0.19 percent. Likewise, we estimated the reproducibility of the LOF determination with 13 discs prepared from the same rock; the mean LOF value in this study was 4.34 percent with an absolute standard deviation of 0.17 percent.

For rocks that behave ideally during fusion, the LOF value is obtained from equations [2] and [9] or directly from equation [10] with $g_N=1$. Thus:

$$Wa = B^O - D \qquad [11]$$

The accuracy of the LOF determination was assessed by comparison of LOF results with wet chemical loss-on-ignition (LOI) values for the same rocks. Table 1 contrasts LOF values, calculated with equation [11], with LOI values for a variety of low-sulfur silicate and carbonate rocks. Inasmuch as the statistical disparities between the LOF and LOI values are of the same magnitude as the statistical precision in the LOF determination, the systematic error in the LOF determination relative to LOI can be assumed to be negligible. Table 2 shows results similar to those in Table 1 for rocks that contain low to significant amounts of sulfide. The LOF values in Table 2 were calculated with equation [10] with the gravimetric factor for sulfide oxidation ($g_S=3$). The close systematic agreement between the LOF and chemistry results is graphically apparent in figure 4 in which the LOF values are plotted against the LOI values for rocks which range from low sulfide to significant sulfide levels. The scatter of points around the 45 degree line in figure 4 indicates negligible systematic error in the LOF measurement for the variety of rocks studied.

DISCUSSION AND SUMMARY

The LOF technique provides a means for assessing the total volatile content of geologic materials; the results are reproducible and in good agreement with volatility values determined by wet-chemical methods. We have identified two classes of fusion chemistry behavior. In the first class, the chemistry is well behaved, and the chemical reactions are gravimetrically similar to those experienced by the blank. In the second, a component of the sample undergoes gravimetric alteration that is not reflected by the blank, a behavior that invites the following questions: (a) is the LOF method reliable for rocks of unusual chemistry that is unknown at the time of analysis, (b) can errors due to such unusual chemistry be detected in a routine operation, and (c) can corrections be made to the LOF measurement on a routine basis?

In the course of our application of the LOF technique to the analysis of many hundreds of rocks, we have had complete success in detecting erroneous LOF values where such values resulted from mass alteration reactions in the fusion procedure that were not accounted for by the blank. These problem samples were identified almost exclusively by the total of the XRF and LOF values for the analysis, an independent measure that will always fall below the range of statistically acceptable numbers if excess oxidation had taken place in the fusion melt. In many examples, low chemistry totals, and therefore low LOF values, have signalled the presence of highly oxidizable species in the sample that were otherwise not expected. Commonly, such species include sulfide and ferrous iron.

From the thermogravimetric data of this study, we have successfully identified the nature of mass alteration reactions as excess oxidation relative to the blank, the number of such reactions, the particular species exhibiting excess oxidation, and the specific oxidation reactions. We have found that sulfide is retained quantitatively as sulfate, a phenomenon which permits the X-ray fluorescence determination of sulfide in a rock sample prepared by a conventional fusion procedure. The questions still remain, however, whether other oxidation states of sulfur are partially or totally lost as volatile oxides during fusion and how we should interpret the determination of sulfur for a mixture of oxidation states. We are presently exploring these questions by Thermogravimetric analysis and Differential Scanning Calorimetry.

In summary, the LOF method described in this report, which is based on simple mass balance considerations, has provided valuable volatility information on samples submitted for X-ray fluorescence analysis. Most silicate and carbonate rocks are well behaved, exhibiting fusion chemistry similar to the chemistry of the reference blank. Less than well behaved samples are easily detected and, where necessary, LOF values can be corrected. Finally, the LOF value summed with the XRF results provides a valuable check on the accuracy of the total analysis. Because the LOF technique is simple and rapid and requires almost no extra expense, we recommend the the LOF method for routine analysis of geologic materials submitted for XRF analysis for which a fusion procedure is needed.

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TABLE 1. Comparison of LOF and LOI values and total composition for low sulfur silicate and carbonate rocks.

Sample Number	Rock Type	Volatile Content(%)		Total	
		LOF	Chem**	XRF + LOF	XRF + Chem**
M128936	Diorite	1.2	1.2	99.50	99.50
M138937	Diorite	1.0	1.1	99.88	99.98
M138940	Diorite	4.2	4.2	99.99	99.99
M138942	Diorite	4.6	4.67	99.59	99.66
M138944	Diorite	2.3	2.1	99.66	99.46
M126437	Andesite	1.23	1.23	99.83	99.83
M126466	Andesite	1.60	1.65	100.0	100.06
M126476	Andesite	1.10	1.12	100.22	100.24
M126477	Andesite	.90	.98	100.04	100.12
M126478	Andesite	1.62	1.62	99.74	99.74
M126480	Andesite	1.20	1.18	99.56	99.54
M126482	Andesite	.90	.96	99.66	99.72
M131858	Andesite	3.10	3.10	99.40	99.40
M132769	Andesite	.40	.39	99.51	99.50
M132773	Andesite	.66	.66	99.55	99.55
M126452	Basalt	.50	.52	99.71	99.73
M126454	Basalt	.06	.06	99.57	99.57
M126457	Basalt	.56	.59	99.94	99.97
M126461	Basalt	1.0	.93	100.51	100.42
M126467	Basalt	.45	.45	99.80	99.80
M126470	Basalt	.70	.74	100.14	100.18
M126473	Basalt	.50	.54	99.37	99.41
M126474	Basalt	.90	.82	99.41	99.33
M126479	Basalt	.55	.55	98.93	98.93
M131829	Basalt	.80	1.00	98.66	98.86
M131832	Basalt	.50	.69	98.29	98.48
M131834	Basalt	.60	.63	100.39	100.42
M131836	Basalt	1.50	1.65	100.12	100.27
M129452	Basalt	1.80	1.67	99.87	99.74
M129453	Basalt	5.10	5.20	100.30	100.40
NBS-1a	Carbonate	34.45	34.55*	--	--
400	Carbonate	47.51	47.40[a]	--	--
401	Carbonate	43.15	43.28	--	--
402	Carbonate	42.73	42.97	--	--
403	Carbonate	44.49	44.76	--	--

*-Bureau of Standards, Certificate of Analyses
**-Penfield Method
a-Ingamells and Suhr, 1967

TABLE 2 Comparison of LOF values calculated by equation [10] with LOI values

for sulfur containing rocks.

Laboratory Sample No.	Total S%	Volatile Contents (%)		
		LOF Eqn.(11)	LOF Eqn. (10)	Chemistry
M132885	.049	5.17	5.27	5.27
M132886	2.20	-2.70	1.71	1.71
M132887	2.94	-1.04	5.24	5.24
M132888	.18	1.06	1.43	1.43
M132889	2.08	-2.41	1.58	1.58
M132890	2.83	-3.76	1.90	1.90
M132891	0.007	5.96	6.16	6.16
M132892	0.005	6.91	6.91	6.91

FIGURE CAPTIONS

Fig. 1. Plot of net gravimetric factor for a variety of rock types as a
         function of sample index.

Fig. 2   Modeling of thermogravimetric alterations of sulfur (cf. Eqn. 10.).

Fig. 3. Modeling of thermogravimetric alterations of MNO (cf. Eqn. 10.).

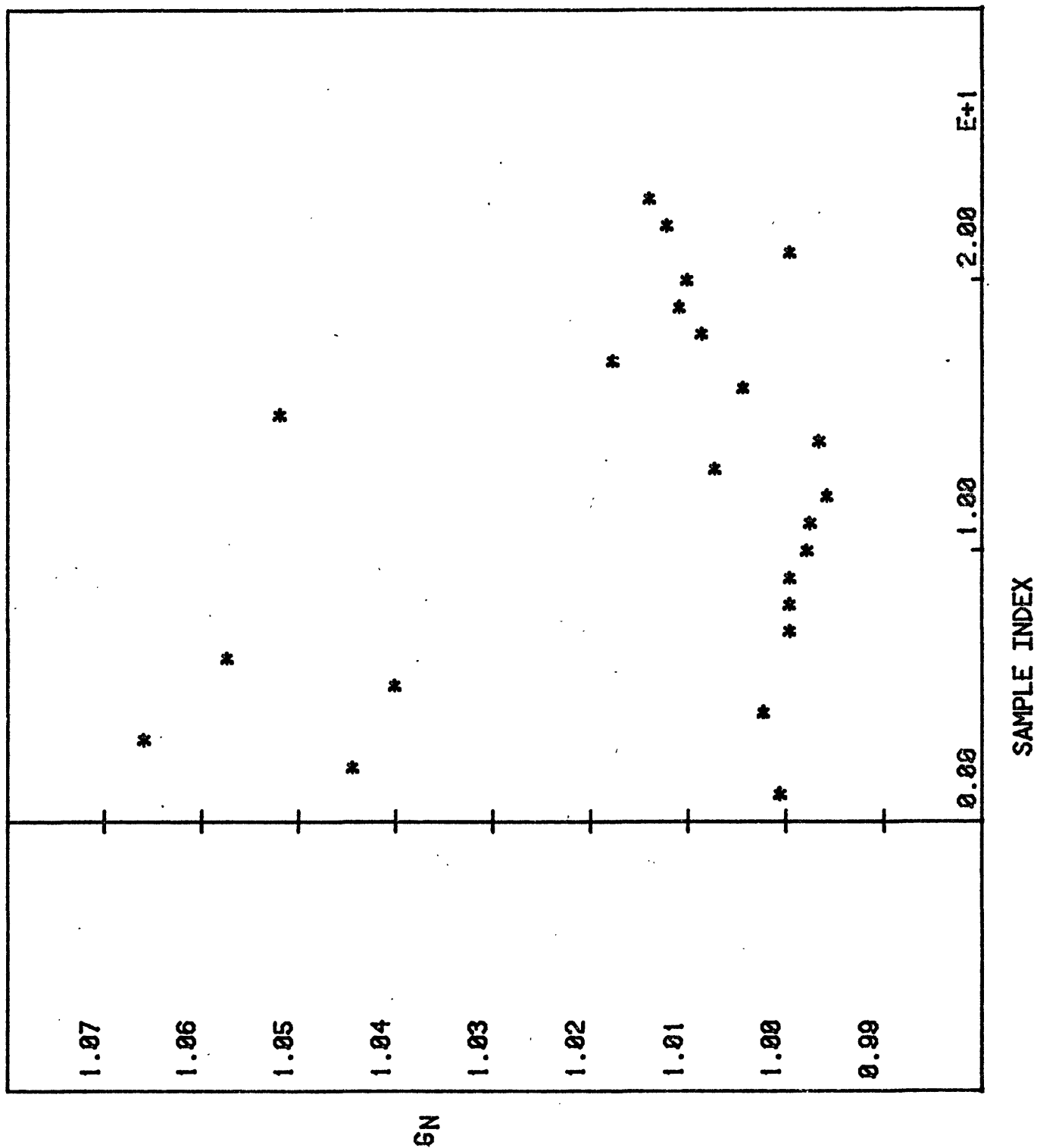Fig. 4. Plot of LOF values vs. LOI values as a check for systematic disparity
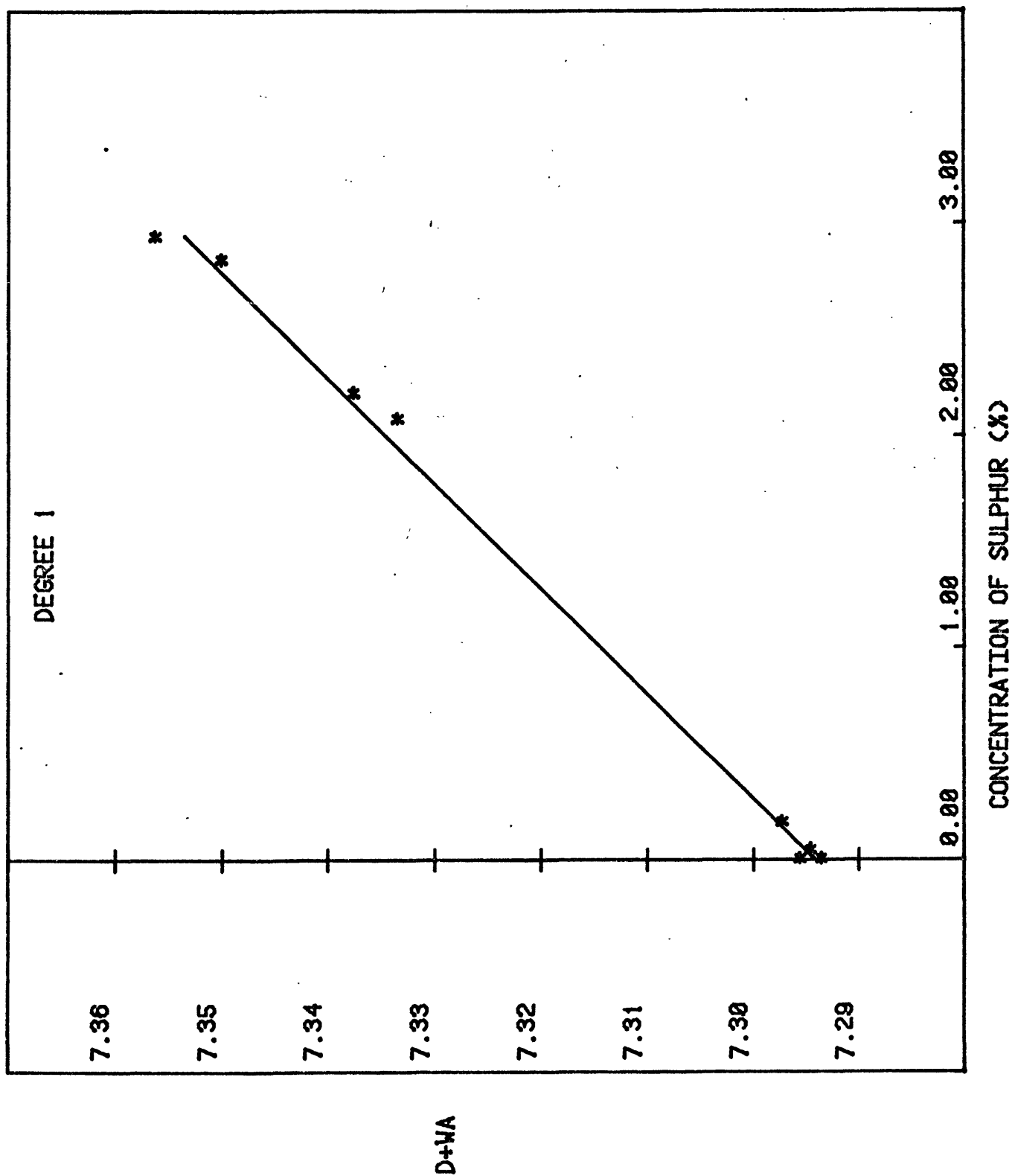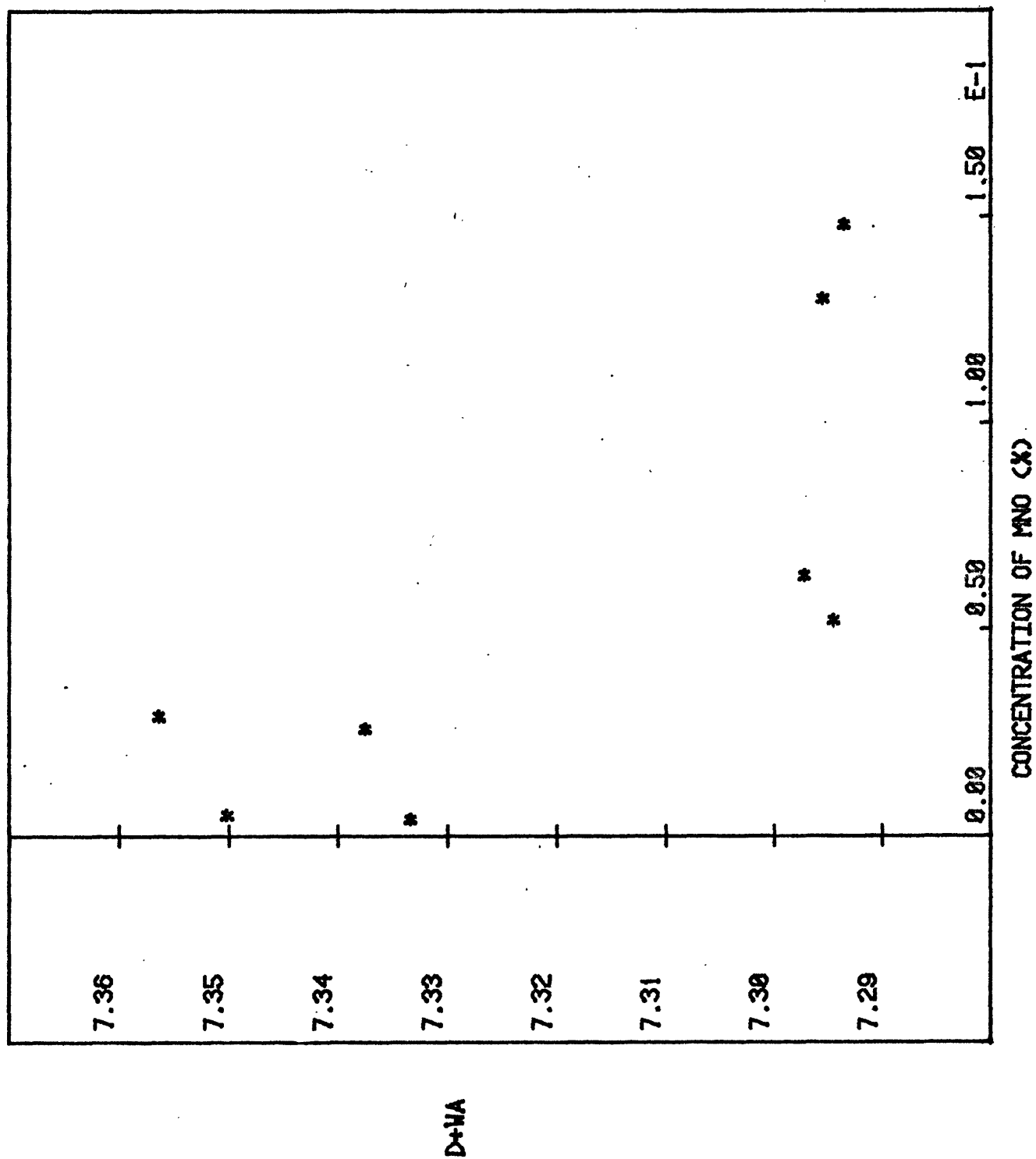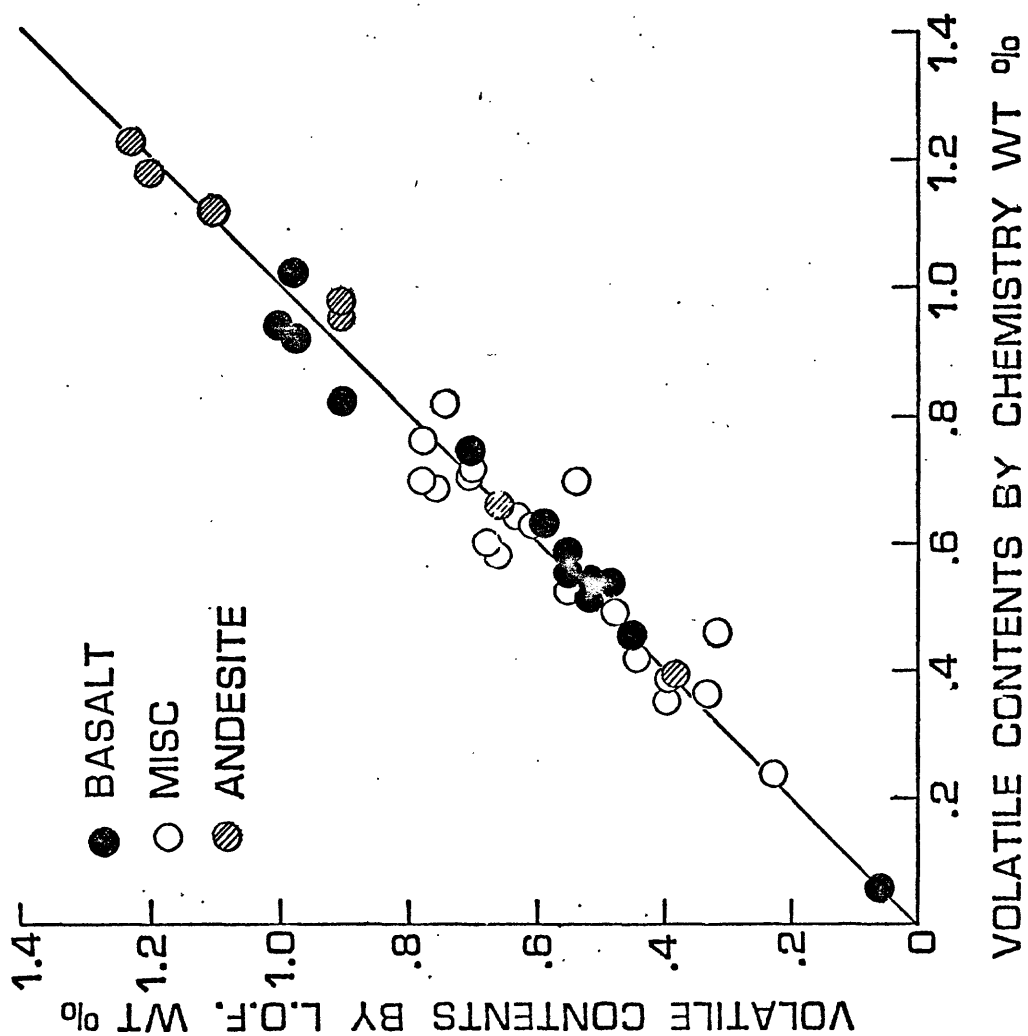   in measurements.

FIG. 1

FIG. 2

FIG. 3

FIGURE 4.