

INTERPRETATION OF CHEMICAL ANALYSES OF MONTMORILLONITES

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ABSTRACT

Particles of montmorillonite representing a considerable range of sizes were separated from crude bentonites by means of sedimentation and supercentrifugation. Except for the effect of impurities, it was found that base-exchange capacity was independent of particle size.

The ratios of the several exchangeable cations on the montmorillonites vary widely as they occur in the crude bentonites. Sodium is the dominant cation in the Clay Spur, Wyoming, and Belle Fourche, South Dakota, samples; calcium in those from Polkville, Mississippi, Santa Rita, New Mexico, Chambers, Arizona, and Plymouth, Utah; in the Little Rock, Arkansas, sample, hydrogen is the most abundant exchangeable cation. The hydrogen ion is reflected in the low pH of the sample. The Otay, California, and Merritt, British Columbia, samples contain more nearly equal amounts of exchangeable calcium, magnesium, and sodium.

Formulae calculations indicate that these samples present a rather wide range in isomorphism and, in consequence, the source of the negative charge on the lattice is widely variable. However, the calculated charges depend, to a large extent, on the purity of the sample. Evidence is presented that silicon dioxide in some form is the most abundant impurity and that significantly large amounts of uncombined silicon dioxide may be present in the finest fractions. The Merritt, British Columbia, sample was found to contain about 35 percent cristobalite. The corresponding particle size fraction from Amory, Mississippi, bentonite contains considerable hydrous mica. Unless allowance is made for impurities, the calculated lattice positions of the electro-positive atoms, and therefore the formula derived therefrom, are essentially meaningless.

Introduction. Ross and Hendricks (1945), Kerr and his associates (1950, 1950a) and other workers have found that hand-picked samples of montmorillonites obtained from bentonite deposits usually contain impurities. For this reason an attempt was made to separate montmorillonite from associated impurities in bentonites by sedimentation and centrifugation with a Sharples Supercentrifuge. By these two methods, samples of montmorillonite of fairly high purity were obtained. Hand-picked samples of 10 different air-dry bentonites were passed through a pulverizer and almost completely sodium-saturated by leaching with neutral-normal sodium acetate. This was done in order to facilitate dispersion. The occluded sodium acetate was removed by washing with neutral 80 percent methanol. The clay was then dispersed in distilled water, transferred to 2000 ml cylinders and allowed to settle 10 minutes. The suspension was removed and allowed to settle overnight. The suspended clay particles were siphoned off and passed through a Sharples Supercentrifuge operated at various speeds up to a maximum of 50,000 rpm. By this means, several clay fractions of different particle sizes, as calculated by Hauser's modification of Stoke's law, were obtained. These were:

- 1600 millimicrons-500 millimicrons
- 500 millimicrons-300 millimicrons
- 300 millimicrons-200 millimicrons
- 200 millimicrons- 70 millimicrons
- 70 millimicrons- 50 millimicrons

Base-exchange capacities were determined on all fractions. Chemical analyses were made on the 200 millimicrons-70 millimicrons fractions. The amount obtained of the 70 millimicrons-50 millimicrons fractions was insufficient for all the analytical determinations. All samples were dried at 85°C before analysis.

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Exchangeable Cations and Base-exchange Capacity on the Original Bentonites. For comparison with the more or less purified sodium-saturated clays, the exchangeable cations, soluble anions and base-exchange capacities were determined on the original hand-picked samples dried at 85°C. The results are shown in table 1.

Attention is called to the wide variation of the cations and anions in the 10 bentonites. Because of the relatively large amounts of soluble anions found in certain samples, it is difficult to state the exact amounts of individual exchangeable cations which they contain; nevertheless, the large variation from sodium to calcium to magnesium gives strong evidence of substantial differences in the environmental conditions to which these bentonites have been subjected in the natural state.

The samples from Belle Fourche, South Dakota,¹ and Clay Spur, Wyoming, are largely sodium clays; those from Polkville, Mississippi; Santa Rita, New Mexico; Plymouth, Utah; and Chambers, Arizona, are largely calcium clays; while the Otay, California, and Merritt, British Columbia, samples contain more nearly equal amounts of exchangeable calcium, magnesium, and sodium.

The Little Rock, Arkansas, sample is especially interesting in that it contains nearly 50 milliequivalents of exchangeable hydrogen ions. Dr. Margaret D. Foster (1951) has described a technique to determine exchangeable hydrogen ions by leaching with neutral-normal ammonium chloride until the leachate gave a yellow color with methyl-red indicator. This technique applied to the Little Rock, Arkansas, sample failed to indicate complete removal of exchangeable hydrogen ions. In our work, this clay was leached with neutral-normal ammonium chloride until an aliquot of the leachate returned to pH 7.0; the exchangeable hydrogen was determined by an electrometric titration of the leachate. By this means it was possible to obtain a good balance between total exchangeable cations and base-exchange capacity as measured by ammonium saturation and distillation.

The last column of table 1 indicates the range of pH of the 10 montmorillonites. It is interesting to note the very low pH, 2.9, obtained on the Little Rock, Arkansas, sample in contrast to the Clay Spur, Wyoming, sample which is predominantly a sodium clay.

Analyses of Montmorillonites. Table 2 shows the chemical analyses of the 200 millimicrons-70 millimicrons fractions of six samples. It should be kept in mind that practically all exchangeable magnesium, as shown in table 1, had been removed by leaching with sodium acetate. Nevertheless, there was almost a threefold variation in magnesium oxide content. The variations in sodium merely reflect differences in base-exchange capacity since the samples were largely sodium saturated. It was found later that practically all the sodium, calcium, and potassium in the samples was exchangeable.

¹ These bentonites were collected by Kerr et al., Columbia University, under the auspices of the American Petroleum Institute (A. P. I. Proj. 49), except for the samples from Plymouth, Utah, and Merritt, British Columbia, which were obtained through Dr. D. W. Thorne, Department of Agronomy, Agricultural Experiment Station, Logan, Utah, and from Dr. H. S. Spence, consulting mineral technologist, Ottawa, Canada, respectively.

Table 1. Base-exchange determinations on untreated montmorillonite clays.

Location	Cations me./100g.					Anions me./100g.			Base-exchange capacity cations-anions	Base-exchange capacity NH ₄ ⁺ dist.	pH ¹
	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	H ⁺	SO ₄ ⁻⁻	Cl ⁻	CO ₃ ⁻⁻			
Merritt, British Columbia.....	23.88	1.49	32.50	10.00			7.80	3.50	56.57	57.5	7.5
Santa Rita, New Mexico.....	2.26	1.91	62.9	29.0					96.07	97.6	7.9
Belle Fourche, South Dakota..	84.80	1.70	7.86	8.50		18.30	5.70		78.86	79.8	8.4
Little Rock, Arkansas.....	1.29	1.27	2.14	22.50	48.70				75.90	78.8	2.9
Polkville, Mississippi.....	2.00	1.00	95.30	21.00			1.60		117.70	113.7	8.1
Amory, Mississippi.....	1.09	2.76	70.00	28.00		1.70		29.00	71.15	71.4	6.1
Otay, California.....	40.70	1.27	20.00	70.40		1.50	8.40		122.47	122.5	6.9
Plymouth, Utah.....	0.45	1.36	99.00	39.00				33.00	106.80	111.8	8.3
Clay Spur, Wyoming.....	82.60	1.74	12.45	8.80		13.00	3.60	10.50	78.49	75.5	9.5
Chambers, Arizona.....	5.50	1.20	100.00	20.00		1.00	4.40	2.00	119.30	117.8	8.5

¹ pH determined on 1 to 10 suspension in distilled water.

Table 2. Analyses of six montmorillonites. (200 millimicrons — 70 millimicrons)
(Artificially saturated with Na⁺)

	Belle Fourche, South Dakota	Clay Spur, Wyoming	Plymouth, Utah	Chambers, Arizona	Polkville, Mississippi	Otay, California
SiO ₂	61.12	61.47	58.60	61.16	63.42	63.04
Al ₂ O ₃	23.10	22.17	20.64	20.38	19.44	18.44
Fe ₂ O ₃	4.37	4.32	4.89	3.66	1.87	1.20
TiO ₂	0.09	0.09	0.57	0.37	0.32	0.14
MnO.....	trace	trace	0.03	0.03	0.00	0.01
P ₂ O ₅	0.05	0.02	0.02	0.03	0.04	0.05
CaO.....	0.24	0.14	0.64	0.14	0.11	0.08
MgO.....	2.50	2.73	4.00	4.52	5.00	7.30
Na ₂ O.....	2.90	3.18	3.00	3.70	3.46	3.40
K ₂ O.....	0.04	0.03	0.07	0.04	0.08	0.02
H ₂ O.....	5.84	6.02	7.63	6.40	6.15	6.47
Total.....	100.25	100.17	100.09	100.43	99.89	100.15

Table 3. Calculated distribution of cations in lattice positions.

	Belle Fourche, South Dakota	Clay Spur, Wyoming	Plymouth, Utah	Chambers, Arizona	Polkville, Mississippi	Otay, California	
	Charge	Charge	Charge	Charge		Charge	
Tetrahedral.....	Si 7.734	Si 7.758	Si 7.638	Si 7.758	Si 8.006	Si 7.957	
	Al .266 —.266	Al .242 —.242	Al .362 —.362	Al .242 —.242		Al .043 —.043	
	8.000	8.000	8.000	8.000		8.000	
Octahedral.....	Al 3.116	Al 3.055	Al 2.808	Al 2.804	Al 2.892	Al 2.700	
	Fe .408 —.502	Fe .410 —.579	Fe .479 —.613	Fe .349 —.845		Fe .178	Fe .114
	Mg .463	Mg .513	Mg .763	Mg .848		Mg .940	Mg 1.340 —.878
	3.987 —.768	3.978 —.821	4.049 —.975	4.001 —1.087	4.010	4.154 —.921	
Interlayer.....	Na .698	Na .778	Na .758	Na .909	Na .846	Na .832	
	K .006 +.768	K .005 +.821	K .011	K .006		K .013	K .003
	Ca .032	Ca .019	Ca .089 +.975	Ca .019 +1.085		Ca .014	Ca .011 +.921
			Mg .014	Mg .066			Mg .032

Table 4. Distribution of charges on lattice layers of six sodium-saturated montmorillonites after deducting soluble SiO₂ and Al₂O₃.

	Belle Fourche, South Dakota		Clay Spur, Wyoming		Plymouth, Utah		Chambers, Arizona		Polkville, Mississippi		Otay, California	
	Charge		Charge		Charge		Charge		Charge		Charge	
Tetrahedral	Si 7.539		Si 7.671		Si 7.465		Si 7.692		Si 7.885		Si 7.900	
	Al .461	-.461	Al .329	-.329	Al .535	-.535	Al .308	-.308	Al .115	-.115	Al .100	-.100
	8.000		8.000		8.000		8.000		8.000		8.000	
Octahedral	Al 3.068		Al 3.032		Al 2.692		Al 2.748		Al 2.788		Al 2.643	
	Fe .456		Fe .431		Fe .543		Fe .383		Fe .202		Fe .120	
	Mg .516	-.396	Mg .539	-.533	Mg .864	-.567	Mg .929	-.749	Mg 1.067	-.896	Mg 1.419	-.873
	4.040		4.002		4.099		4.060		4.057		4.182	
Interlayer	Na .779		Na .816		Na .858		Na .996		Na .961		Na .880	
	K .007		K .005		K .013		K .007		K .015		K .003	
	Ca .036	+.858	Ca .020	+.861	Ca .101		Ca .020		Ca .017	+1.010	Ca .011	
					Mg .015	+1.103	Mg .007	+1.057			Mg .034	+ .973

Interpretation of Analyses. The data in table 2 were calculated by the method outlined by Kelley in the preceding paper. The results are shown in table 3. Attention is directed to four points that are illustrated by these calculations. Firstly, in all samples except the Polkville montmorillonite there is not enough silicon to fill all tetrahedral positions. Accordingly, aluminum is assigned to tetrahedral positions in amounts just sufficient to fill the remaining position. Secondly, the ratio of tetrahedral charge to octahedral charge varies quite widely. As analyzed, it would appear that the Otay sample contains very little tetrahedral aluminum, while in the Belle Fourche and Clay Spur samples approximately one-third of the calculated charge appears to originate in the tetrahedral layers of the lattice. Thirdly, the total octahedral cations approximate four per lattice unit in five of the montmorillonites, but exceeds four in the Otay sample by an amount considerably in excess of the probable error of analysis. Finally, the total octahedral cations slightly exceeded four per lattice unit in the Polkville sample, but were found to be somewhat less than four in the Belle Fourche and Clay Spur samples.

As samples separated from certain other bentonites undoubtedly contain uncombined silicon dioxide, or silica, an attempt was made to ascertain whether the aforementioned samples contain such impurity. On extraction with 0.5 normal-sodium hydroxide it was found that silica was dissolved in amounts ranging from 3.6 to 8.4 percent, and aluminum oxide, or alumina, in amounts ranging from 0.6 to 2.25 percent.

Accordingly, the analyses were recalculated on the assumption that the silica and alumina removed by sodium hydroxide were present as impurities and not as a part of the clay lattice. These results are reported in table 4. As will be seen, tetrahedral aluminum, and therefore tetrahedral charge, was increased substantially in every case. Consequently, the ratios of the charges are influenced considerably. The calculated total octahedral cations exceeded four in every case, and in the Otay sample was 4.182.

It was not proven definitely that all the silica and alumina removed by sodium hydroxide was impurity. However, in view of the very small amount of alumina and the larger amount of silica removed from certain

samples, it is at least possible that the major part was impurity.

There is no direct evidence that iron is present as an impurity. However, from the total iron present in most of these clays, it seems unlikely that all of it can be assigned to the lattice. For example, examination of hand-picked samples of Polkville montmorillonite show small rosette-like areas, apparently of iron stain, dispersed at random in a white clay. Yet the chemical determination of iron does not differentiate lattice from non-lattice iron. Sodium hydroxide would not dissolve iron present as an impurity. At present it can only be concluded that the iron content in these samples is quite variable, ranging from 1.2 percent to 4.89 percent.

Samples Containing Cristobalite. When one attempts to calculate the analysis of the 200 millimicrons-70 millimicrons fraction from the Santa Rita and that from the Merritt bentonites, it becomes apparent at once that these samples contain substantial amounts of silica as impurity. Table 5 shows the chemical analyses and the calculated results on these two samples. Mere inspection of the analyses suggests impurities of some sort. This is indicated by the exceptionally high silica content in the Merritt sample and by the somewhat elevated silica content of the Santa Rita sample. The calculated results confirm this beyond any reasonable doubt, as shown by two facts: (1) the total calculated silicon ions exceed eight per lattice unit in both cases and markedly so in the case of the Merritt montmorillonite, and (2) the total octahedral cations are substantially less than four per unit. These two criteria establish beyond reasonable question that, although all the coarser grained materials had been eliminated, each of these two samples still contained some form of silica as impurity, and in substantial amounts.

X-ray analyses by Dr. J. H. Milne of our laboratories revealed the presence of cristobalite in each of these samples. Accordingly, an attempt was made to remove cristobalite by extraction with 0.5 normal sodium hydroxide. It was found that silica was dissolved to the extent of 7.5 percent in the Santa Rita sample and 29.9 percent in the Merritt sample. Only a small amount of alumina was dissolved, 0.86 percent in the Santa Rita

Table 5. Chemical analyses and calculated results on Santa Rita, New Mexico and Merritt, British Columbia samples. (200 millimicrons — 70 millimicrons)

Santa Rita, New Mexico			Merritt, British Columbia		
Analysis	Calculation		Analysis	Calculation	
SiO ₂ 65.21	Tetrahedral Si	8.141	SiO ₂ 71.60	Tetrahedral Si	8.818
Al ₂ O ₃ 19.13			Al ₂ O ₃ 15.75		
Fe ₂ O ₃ 1.07	Octahedral Al	2.815	Fe ₂ O ₃ 3.78	Octahedral Al	2.285
CaO 0.04	Fe	.101	CaO 0.07	Fe	.351
MgO 4.57	Mg	.850	MgO 0.97	Mg	.178
		3.766			2.814
Na ₂ O 3.90	Interlayer Na	.943	Na ₂ O 1.88	Interlayer Na	.448
K ₂ O 0.14	K	.022	K ₂ O .09	K	.015
*MgO 0.066	Mg	.012			
	Ca	.005			

* Exchangeable magnesium.

specimen and 0.68 percent in the Merritt montmorillonite. These results strongly indicate that the crystals of montmorillonite in these two samples were only slightly, if at all, attacked by sodium hydroxide.

After correcting these analyses for the silica and alumina dissolved by sodium hydroxide, the data were recalculated. The results still showed less than four cations per lattice unit, indicating that not all of the cristobalite had been removed.

Consequently, uncombined silica was determined in the Merritt sample by the phosphoric acid method of Talvitie (1951). This method showed that 37.65 percent of the sample was cristobalite.

After correcting the analysis for cristobalite as found by the phosphoric acid method and subtracting alumina soluble in sodium hydroxide, the data were recalculated as shown in table 6. The recalculated data on the Santa Rita sample corrected for silica and alumina dissolved by sodium hydroxide are also shown.

Table 6. Distribution of charges in Santa Rita, New Mexico and Merritt, British Columbia montmorillonite samples after deducting SiO₂ and Al₂O₃. (200 millimicrons—70 millimicrons)

Santa Rita, New Mexico			Merritt, British Columbia		
	Charge			Charge	
Tetrahedral-----Si	7.930		Tetrahedral-----Si	7.308	
Al	.070	---.070	Al	.692	---.692
	8.000			8.000	
Octahedral-----Al	2.912		Octahedral-----Al	3.131	
Fe	.112		Fe	.612	
Mg	.943	---1.042	Mg	.311	---.149
	3.967	---1.112		4.054	---.841
Interlayer-----Na	1.048		Interlayer-----Na	.784	
K	.025		K	.024	
Ca	.006		Ca	.016	+ .840
Mg	.014	+1.113			

It will be noted in the Santa Rita sample that the total calculated octahedral cations were still less than four per lattice unit, indicating that not all of the cristobalite had been removed. On the other hand, the data

for the Merritt sample gave a fully rational lattice, with slightly less than eight silicons and somewhat more than four total octahedral cations per lattice unit.

Assuming 37.65 percent impurities in the case of the Merritt sample, the base-exchange capacity of the purified material would be approximately 106 milliequivalents, which is in agreement with those of Belle Fourche, Clay Spur, Plymouth, Polkville, Chambers, and Otay. The base-exchange capacity of the unextracted sample was approximately 65 milliequivalents.

The sample from Little Rock also contains a small amount of cristobalite as found by the X-ray method. The calculated formula accordingly showed a deficiency of octahedral cations.

Sample Containing Hydrous Mica. By X-ray analysis, Dr. I. H. Milne found hydrous mica present in the 200 millimicrons-70 millimicrons fraction of the Amory montmorillonite. Moreover, this conclusion is supported by the chemical analysis which showed 0.63 percent potassium, of which only 0.07 percent is exchangeable.

Relation of Base Exchange to Particle Size. The data shown in table 7 afford evidence that base-exchange capacity of a pure montmorillonite is independent of particle size. This is also illustrated by the results obtained on the Plymouth, Polkville, Chambers, and Otay montmorillonites. Their base-exchange capacities are, in each case, nearly constant over five particle-size fractions. Conversely, the samples from the other localities show more or less increase in base-exchange capacity from the coarse to the finest fractions. The implication is that the coarser fractions may contain more impurity. The last column of the table shows the percentage increase in base-exchange capacity of the 200 millimicrons-70 millimicrons fraction over that of the original bentonite. It is interesting to note that with the Clay Spur sample which is often referred to as a typical montmorillonite, the increase in base-exchange capacity was approximately 36 percent, indicating that a hand-picked sample of this montmorillonite can be grossly impure.

It is also interesting to note that those montmorillonites with base-exchange capacities of 100 milliequivalents or more in the crude state apparently contain the least impurity.

Conclusion. The foregoing data afford strong evidence that the 200 millimicrons-70 millimicrons fraction of certain clays contains substantial amounts of impurities. In the case of the Merritt and Santa Rita samples, and possibly others, it is concluded that impurities not removed by gravitational methods must be determined by analytical methods before the interpretation of clay properties can be made. Sedimentation and centrifugation will separate montmorillonite from the coarser types of associated substances, but there appears to be little hope of removing all forms of extraneous silica by any means other than by some chemical solvent followed by an analytical determination of the impurity.

Finally, the foregoing data show that the calculated isomorphism of these samples is substantially modified by impurities. In general, silica as impurity accentuates the octahedral charge and reduces that of the tetrahedral layer. In other words, the calculated isomorphism may

Table 7. Base-exchange capacities of montmorillonites in relation to particle size.
(me./100 g of clay on a dry weight basis at 85°C)

Montmorillonite sample	Particle size					Untreated clay sample	Base-exchange capacity increase 200-70m μ fraction / crude Percent
	1600-500m μ	500-300m μ	300-200m μ	200-70m μ	70-50m μ		
Merritt, British Columbia.....	47.0	60.0	67.3	65.9	69.7	57.5	14.7
Amory, Mississippi.....	58.8	72.9	80.8	84.7	84.0	71.4	18.6
Little Rock, Arkansas.....	81.6	86.4	86.8	86.8	86.0	78.8	10.0
Belle Fourche, South Dakota.....	50.6	94.6	97.9	94.2	97.9	79.8	18.0
Clay Spur, Wyoming.....	84.2	97.2	95.0	103.0	101.6	75.5	36.7
Santa Rita, New Mexico.....	73.0	114.1	116.5	117.0	118.5	97.6	20.0
Plymouth, Utah.....	117.6	119.0	116.5	118.4	121.6	111.8	5.9
Polkville, Mississippi.....	118.0	119.0	119.5	121.8	118.4	113.7	7.0
Chambers, Arizona.....	125.3	123.5	122.6	124.0	130.5	117.8	5.3
Otay, California.....	127.5	126.0	127.5	128.3	123.0	122.5	4.7

m μ = millimicrons.

be greatly influenced by the impurities that occur in montmorillonites. The data presented in this paper afford strong evidence that insistence on high purity in the interpretation of chemical analysis is amply justified. Unless the sample is largely free from silica as impurity there is bound to be uncertainty as to the actual isomorphism in the sample, and therefore, there will be reasonable doubt as to the origin of the charge.

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DISCUSSION

C. S. Ross:

With reference to the analyses of granite and diabase that Kelley cited, there are two schools of thought on their evaluation. No matter how bad they may appear by mere inspection, one group feels they should be lumped together with the good analyses and run through a mathematical hokus-pokus and be a part of the final result of the mean. The other school believes analyses that appear to be bad should be eliminated. When the poor analyses mentioned by Kelley are eliminated most of the rest group very nicely around the means. I think that it is justifiable to throw out an analysis where common sense indicates that somebody blundered.

W. P. Kelley:

It is perfectly true that the vast majority of the analyses cluster around a fairly close median point. However, when an analysis is published, how does one know whether it is a good analysis or a bad one? I repeat, we are not justified in making dogmatic assertions about the specific isomorphism when calculated from a single analysis.

R. A. Rowland:

Has Osthaus applied his technique of analysis to mineral mixtures from sediments or soils?

B. B. Osthaus:

No, we felt that before tackling sediments we had better learn something about simpler systems.

R. A. Rowland:

Eighty percent of the earth crust is made up of clay, and of that 80 percent, 5 percent is clay of hydrothermal origin. Every one of us, including myself, is guilty of choosing a clay of hydrothermal origin or near hydrothermal origin on which to do his detailed work. We choose clays that are perfect examples, or nearly perfect examples, as standards. Yet the very reason for our existence as clay researchers is to learn something of the other 75 percent; and until we do there is only scant justification for our work, except as a purely academic matter.

C. S. Ross:

Though there is need for studying clays of the soils and sediments, we need to start first of all with as pure minerals as we can get before we handle mixtures of minerals.

In our work on the montmorillonite group (1945), it might appear that we used a disproportionate number of bentonite analyses, but that was the best way to secure approximately pure clay materials. The neglect of all the other materials was from necessity and not from choice. The Ordovician bentonites are the best source for potash micas. Here again we would be inclined to use a disproportionate number of samples to the neglect of the potash clay minerals in soils.

I. Barshad:

Besides using chemical analyses for calculating formulae, an analysis, or even the analysis of a single constituent, is of great value for other purposes. An analysis of the free oxides, carbonates, or soluble salts is indispensable for the classification of soils. In the study of clays an analysis of the total potassium or calcium content in samples, which were saturated with Na⁺ or NH₄⁺ prior to analysis, may indicate a great deal about the presence of hydrous mica or such impurities as the feldspars.

In this discussion not enough stress was placed on the distinction between the qualitative and the quantitative aspects of the analysis. Thus for a qualitative analysis of a sample, the use of any one of the methods may suffice, but for a quantitative analysis of the same sample several of the methods may be required. Therefore, thorough understanding of all of the methods is essential for an accurate analysis.

H. R. Shell:

The person desiring a chemical analysis should first make absolutely sure that he has a sample which, if analyzed correctly, will

give results that directly pertain to the problem at hand. Further, he should collaborate with the analyst by stating (1) the elements or constituents to be determined, and (2) the absolute accuracy which must be obtained for each individual element or constituent. A complete analysis is usually not economically feasible. All samples for scientific or research purposes should be analyzed (1) at least in duplicate, and (2) in conjunction with similar samples of known composition, such as those obtainable from the U. S. Bureau of Standards or the U. S. Geological Survey.

The analytical chemist, if at all possible, should use methods that are specific, and should guide his work with spectrographic analysis. Interfering elements, such as P and F, should be checked unless they are previously known to be absent. F is especially important in minerals where F⁻ may substitute for OH⁻, for example, in various micas and amphiboles.

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