IV Vuursteenanalyse

Application of chemical analysis in the classification of archaeological silicate samples

H. A. Das

SUMMARY
The use of chemical analysis for classification purposes of silicate samples depends on three conditions:
a) A sufficiently large body of samples, grouped according to archaeological criteria, is available.
b) It is possible to analyze the samples in a purely instrumental way for many constituents simultaneously. The method is not subject to a bias and the produced results have a precision of better than 10%.
c) The concentration ratios expressed in terms of the concentration of a major constituent, are submitted to a simple statistical test.
The validity of the final conclusion is strongly dependent on the choice of the matching criteria.

The archaeologist may find the tub, but altogether mis Diogenes.
Sir Mortimer Wheeler, Archaeology from the earth. Penguin Ltd. 1961, p. 243.

Introduction
Archaeology is primarily a fact-finding discipline. However, it is to be distinguished from science in that its ultimate goal is the revification of the human past. Judged from this point of view, the significance of science applied in archaeology, can only be that it facilitates a conclusion on human achievement.
This sets a severe limit to the importance of chemical analysis. At its best, it can tell us that, with a certain probability, the findings can be divided in a few groups of similar composition. It is by no means certain that this knowledge can be translated into some archaeologically useful conclusion.
There are a few classes of material on which - for different reasons - it may useful to apply chemical analysis.

Material	Type of analysis	Reason
Organic substances	^{14}C measurement	
Bones	Determination of fluorine	Dating
Coins and other Metal objects	Major constituents	Study of ancient technology
	Trace elements	Provenance studies
Silicate samples	Major and minor constituents	Provenance studies
	('chemical finger-printing')	Examination of firing and glazing techniques.

Only the fingerprinting technique, applied to silicates, will be considered here. The aim is to give a concise picture of the current practical approach. The most convenient methods of analysis are the purely instrumental techniques. Among these, neutron activation analysis is the most conspicuous. For details on the experimental techniques, the reader should consult references [1-6].
A complete review of the literature on chemical analysis of archaeological specimens by nuclear methods can be found in the booklet 'Nuclear activation applied to materials of art and archaeology', edited by E.V. Sayre and P. M. Meyers of the Chemistry Department of Brookhaven Laboratory, the Conservation Center of N.Y. University, and the Metropolitan Museum of Art. The publication summarizes the work done until June 1971. From this survey it emerges that attention has been devoted almost entirely to only two types of samples: Pottery and obsidian. No data are available on flint.
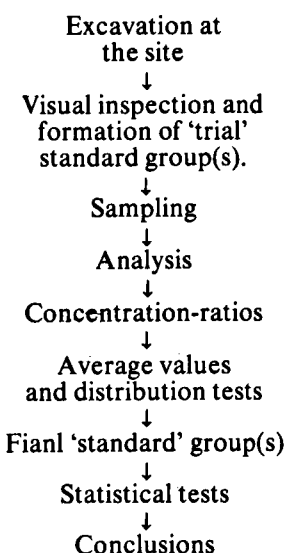
2. Methods

2.1. Outline of the procedure
The complete procedure, from sampling to the final conclusion, can be summarized by the scheme given in table I.

TABLE I

Outline of the procedure

Excavation at
the site
↓
Visual inspection and
formation of 'trial'
standard group(s).
↓
Sampling
↓
Analysis
↓
Concentration-ratios
↓
Average values
and distribution tests
↓
Fianl 'standard' group(s)
↓
Statistical tests
↓
Conclusions

Excavation at the site
At the site, specimens are collected by the archaeologist. They are cleaned and labelled.

Visual inspection and formation of trial 'Standard' group (S)
A selection is made, usually on stylistical grounds, in order to obtain a trial 'standard' group of specimens which seems to be representative for the majority of the specimens, collected at that particular site. It may turn out that several trial groups have to be formed to cover the collection properly.

Sampling
All specimens are sampled. This is usually done by drilling with a diamond-headed dentist's drill. The material is collected in polythene capsules which are properly marked.

Analysis
The samples are analysed by a multicomponent method, preferably purely instrumentally. In chosing the constituents to be analysed, it is advisable to avoid items which are in all probability strongly correlated. As an example, the group of the lanthanides can be mentioned. The elements chosen should be distributed evenly over the periodic table.

Concentration ratios

The concentration-ratios are obtained by chosing one major constituent as reference and dividing the concentrations of all other constituents by that of the reference. Usually iron is chosen for this purpose. The use of ratios instead of absolute concentrations is necessary in the case of pottery, where the body may have been diluted with silica. It is also well-known in soil science. When dealing with a solid rock like flint, the calculation of ratios will not be imperative.

Average value and distribution tests

The average values and the distributions around the averages are calculated for each determined constituent. It is recommended to try the logarithmic as well as the linear frequency distribution. If the result of this test does not confirm the supposed homogeneity of the testgroup(s) the initial sample choice should be adapted now.

Final 'Standard' group(s)

The average values and standard deviations for the final 'standard' group(s) are computed.

Statistical tests

For two reasons, the data processing is never quite rigorous from the mathematical point of view.
a) The variables (the elemental concentrations) are seldom completely independent; nor are the proportions of two elements always constant.
b) It is obvious that some, rather arbitrary, criterion must be applied to decide whether a given specimen will be regarded as pertaining to the standard group.
In section 2.3, two different approaches will be discussed briefly.

2.2. Methods of analysis

The following instrumental analytical techniques can be applied:
- X-ray fluorescence spectrometry [4]
- Emission spectrography [5,6]
- Activation analysis [3]

X-ray fluorescence is limited to the outermost layer of the sample. It this is prepared with due care (pelletizing for powders, polishing for chips), good results can be obtained for the major constituents. Some results obtained in routine analysis at the Geological Survey of Canada are given in table II.

TABLE II

Precision and accuracy of X-ray emission spectrography on fused and pelletized samples

Consti- tuent	Range	Precision		Accuracy	
		Fused	Pelle- tized	Fused	Pelle- tized
Fe_2O_3	0 - 20%	0.20	0.06	0.25	0.4
MnO	0 - 1	0.004	0.005	0.01	0.03
TiO_2	0 - 5	0.012	0.015	0.07	0.05
CaO	0 - 20	0.08	0.10	0.23	0.4
K_2O	0 - 6	0.02	0.03	0.09	0.1
SiO_2	35 - 75	0.78	0.80	1.0	1.2
Al_2O3	0 - 20	0.74	0.30	1.0	1.0
MgO	0 - 40	0.42	0.40	0.56	0.5

The quoted data are standard deviations.

J. A. Maxwell, Rock and Mineral Analysis, Wiley Interscience, N.Y. 1968, p. 515.

Emission spectrography is bases on the registration of the optical line spectrum which is emitted when a material is heated to a sufficiently high temperature (= 4000-5000 °K). It is an excellent technique if a rapid semi-quantitaive scan of a group of samples has to be made. The powdered material is mixed with pure carbon to suppress the matrix-effect, and put in a well-type graphite electrode. The present state of this technique is described in ref.[4]. The sensitivity of the method is good (cf. table III) but the precision is moderate and the accuracy is poor. In general it can be said that the method is not suitable for application in accurate finger-printing of silicates.

TABLE III

Sensitivity of optical emission spectrography

Element	Wave-length	Detection limit
Ag	328.0 nm	0.5 μg.g^{-1}
Al	394.4	1
B	249.8	1
Be	234.8	2
Cd	326.1	50
Co	340.5	5
Cu	327.3	0.1
Fe	302.0	10
Mg	285.2	0.01
Mn	279.4	2
Mo	313.3	5
Pb	283.3	10
Sn	284.0	5
Ti	337.3	5
V	318.4	10
W	294.4	100
Zn	334.5	100

Data taken from: L. de Galan, Analytische spectrometrie.
Argon Elsevier, Amsterdam, 1972, p. 109.

Activation analysis is based on the artificial radioactivity, induced in the sample by irradiation with 'elementary' particles, especially neutrons. It is a useful method for the instrumental determination of 20-30 elements in silicate rocks and sediments. The sensitivity is usually excellent whereas the precision is good. In general matrix effects can be neglected. There are two major drawbacks: The rather long turn-over time and the fact that the method implies the availability of highly sophisticated equipment. The first difficulty is caused by the time-consuming irradiation- and decay-periods. This can be compensated for to some extent by the simultaneous processing of large series of samples. The second limitation implies restriction to some nuclear research centres.
The elements which can be determined instrumentally are listed in table IV.

TABLE IV

Elements which can be determined by instrumental activation analysis

Thermal neutron activation	Na, Al, K, Sc, [V], Cr, Mn, Fe, Co, Zn, Ga, Se, Br, Rb, [Ag], Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, [Gd], Tb, Tm. Yb, Lu, Hf, [Ta], [Au], [Hg], Th, U.
Fast neutron activation	Si
Photon activation	Mg, Ca, Ti, [Ni], Sr, Zr, Nb.
Capture γ-ray measurements	B, Sm, Gd

Elements in brackets are marginal.

Most fingerprinting work has been done by activation analysis.

2.3. Statistical methods
Two approaches will be mentioned here as examples. They are due to I. Perlman and F. Asaro [7[and to O.U. Anders [8]. The method used at Brookhaven National Laboratory is very similar to that of ref. [7].

2.3.1. Perlman and Asaro's method
The difference Δ between the observed value and the mean value for the 'standard' group is divided by the standard deviation σ to obtain the excentricity, u. Using standard statistical tables, the odds are assigned that the sample does not belong to the 'standard' group. The product of the odds, obtained for the various elements, is used as an 'index of disagreement'. A cut-off value of 1000 is used to make the final decision whether a sample belongs or not.

2.3.2. Anders' method
Concentration ratios are formed for each sample by dividing the concentration of *each* element by that of *each* of the elements. One obtains a triangular matrix which is called 'concentration matrix', ^{x}n. Let A, B, C, ... denote the concentrations of the determined elements. The correlation matrix for sample n is then:

$$
x_n = \begin{bmatrix}
1 & \cdot & \cdot & \cdot & \cdots \\
\left(\frac{B}{A}\right)_n & 1 & & & \\
\left(\frac{C}{A}\right)_n & \left(\frac{C}{B}\right)_n & 1 & & \\
\left(\frac{D}{A}\right)_n & \left(\frac{D}{B}\right)_n & \left(\frac{D}{C}\right)_n & 1 & \\
\vdots & & & &
\end{bmatrix}
$$

The ratio matrix, ^{y}n, of the sample and the average of the 'standard' group is now formed. This is done by dividing each of the elements of the concentration matrix of the sample by the corresponding element of the concentration matrix of the sample by the corresponding element of the concentration matrix of the average. Thus one gets:

$$
y_n = \begin{bmatrix}
1 & \cdot & \cdot & \cdot & \cdots \\
\dfrac{(B/A)_n}{(B/A)_{av}} & 1 & & \\
\dfrac{(C/A)_n}{(C/A)_{av}} & \dfrac{(C/B)_n}{(C/B)_{av}} & 1 & \\
\vdots & & &
\end{bmatrix}
$$

If there is a perfect correlation, ^{y}n will be equal to unity. The matching criterion is now introduced as the number $M>1$ in the relation $1/M < ^y$n $< M$. The lower the value of M, the higher the probability that the sample belongs.

3. Examples
The first example is based on the work of I. Perlman and F. Asaro [7]: Table V gives the average data, obtained

for 32 samples of Egyptian 'nile mud' pottery, expressed in terms of the concentrations relative to iron. Two other samples, A and B, are now tested for their relation with this 'standard' group. The results for arsenic are rejected, as being too unreliable. The date on the remaining 15 elements are quite sufficient, however, to draw the conclusion that A is identical with the samples of the 'standard' group, while B is not.

The second application is taken from a study of Miss J. S. Olin and E. V. Sayre [9]. The aim was to determine whether pottery manufactured in North-Devon during the 17th century shows a compositional uniformity.

TABLE V

Comparison of two samples with a 'standard' group

Element	Concentration ratio to Fe in standard group (average ± σ)	Sample A Concentration ratio	Sample A u=Δ/σ	Sample B Concentration ratio	Sample B u=Δ/σ
Mn	$(177 \pm 12).10^{-4}$	17	0.25	105	6.0
Na	0.196 ± 0.031	0.173	0.74	0.125	2.3
U	$(0.33 \pm 0.06).10^{-4}$	0.28	0.83	0.93	10
Lu	$(0.075 \pm 0.05).10^{-4}$	0.071	0.80	0.080	1.0
La	$(4.8 \pm 0.20).10^{-4}$	4.62	0.90	8.2	17
Ti	0.146 ± 0.008	0.142	0.50	0.11	3.5
Sb	$(0.043 \pm 0.010).10^{-4}$	0.040	3.0	0.18	14
As	$(0.13 \pm 0.17).10^{-4}$	0.19	(*)	1.15	(*)
Sc	$(3.38 \pm 0.16).10^{-4}$	3.47	0.56	3.70	2.0
Co	$(5.1 \pm 0.3).10^{-4}$	5.41	1.0	4.0	3.7
Ta	$(0.21 \pm 0.02).10^{-4}$	0.19	1.0	0.22	0.5
Cs	$(0.20 \pm 0.03).10^{-4}$	0.23	1.0	0.72	27
Cr	$(26.5 \pm 2.6).10^{-4}$	26.5	0.0	39.2	4.9
Hf	$(1.27 \pm 0.11).10^{-4}$	1.18	0.82	1.4	1.2
Th	$(1.02 \pm 0.08).10^{-4}$	0.92	0.11	2.04	13
Ba	$(72 \pm 11).10^{-4}$	65	0.64	80	0.73
Rb	$(9 \pm 1).10^{-4}$	7	2.0	12	3.0

(*) Element rejected.

Based on data taken from ref. [7].
Analytical technique: Thermal neutron activation.

TABLE VI

Comparison of two groups of 17th century English pottery

Element	Concentration-ratio to Fe (average ± σ) 'fine' ware	'gravel' ware
Sc	$(2.3 \pm 0.3).10^{-4}$	$(2.0 \pm 0.4).10^{-4}$
La	$(6.2 \pm 0.6).10^{-4}$	$(5.8 \pm 1.0).10^{-4}$
Eu	$(20.1 \pm 2.0).10^{-4}$	$(17.2 \pm 3.7).10^{-4}$
Ce	$(11.8 \pm 1.0).10^{-4}$	$(10.5 \pm 2.5).10^{-4}$
Th	$(10.1 \pm 2.1).10^{-4}$	$(9.4 \pm 2.5).10^{-4}$
Cr	$(9.6 \pm 2.5).10^{-4}$	$(9.1 \pm 2.0).10^{-4}$
Co	$(27.2 \pm 3.0).10^{-4}$	$(24.3 \pm 4.4).10^{-4}$

Data taken from ref. [9].
Analytical technique: Thermal neutron activation.

Table VI gives the average concentrations and the associated standard deviations of two small collections of 'fine' and 'gravel' ware. It can be seen that, judging from these data, the two groups are identical.

4. Conclusion

Two concluding remarks can be made:
a) The role in archaeology of fingerprinting by chemical analysis is modest but not negligible.
b) The most important analytical technique for the classification of silicates is activation analysis.

Petten, april 1975

REFERENCES

[1] J. A. Maxwell - Rock and mineral analysis, Wiley-Interscience, New York, 1968.
[2] A. Volborth - Elemental analysis in geochemistry, Elsevier, Amsterdam, 1969, Part A.
[3] D. de Soete et al. - Neutron activation analysis. Wiley-Interscience, New York 1972.
[4] R. Jenkins and R. L. de Vries - Practical X-ray spectrometry. Springer New York, 1970.
[5] L. H. Ahrens and S. R. Taylor - Spectrochemical analysis, Addison-Wesley, Reading, 1961.
[6] F. J. M. J. Maessen - Thesis Amsterdam, 1975. (Available upon request from the Laboratory for Analytical Chemistry of the University of Amsterdam).
[7] I. Perlman and F. Asaro - Pottery analysis by neutron activation. Archaeometry 11 (1969), 21-52.
[8] O. U. Anders - Ratio matching. A statistical aid for discovering generic relationships among samples. Anal. Chem. 44 (1972), 1930-1933.
[9] J. S. Olin and E. V. Sayre - Compositional categories of English and American pottery of the American colonial period.
Chapter 14 in Science and Archaeology, R. H. Brill ed. MIT Press, Cambridge Mass., 1971, P. 196-209.