

NEUTRON ACTIVATION ANALYSIS OF ARCHAEOLOGICAL CERAMICS AND RELATED PROBLEMS

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It is a curious thing to see how rarely the question of ceramics origin is asked in archaeological literature. Its historical importance needs no demonstration; however, it can appear as a meaningless question, quite often, in absence of any indication.

That led Anna Shepard (Brongniart, 1842) to choose as a base of classification of ceramics, a geometric description. More recently the code for description of ceramics proposed by Gardin (Fouque, 1869) takes the same point of view with addition of a detailed coded analysis of shape.

We know about some noteworthy exceptions like the Hellenistic amphorae that bear stamps mentioning their origin: Thasos, Rhodos, etc., or terra sigillata for example. But the general case is that information about origin is simply lacking.

It can be understood that archaeologists do not put any systematic effort in search for the production sites; but in case we decide to classify a certain type of ceramics into origin classes, using chemical analysis, there is no choice: we must build up reference groups of composition, corresponding to known origins, and we cannot escape the problem of searching at least the most important workshops, or production zones.

It enables us to give a definition of a ceramics that is not only useful for the sake of practical necessity of our technique, but is also a step forwards for archaeology itself, to put it back to an historical view instead of an abstract classification. We can say that ceramics are, since the most remote times, artefacts made in order to satisfy some basic social needs like storage and transportation, mostly of food, cooking, eating and drinking.

They were made, according to the state of division of work of society, and of differentiation of needs, by everybody or by professionals. The choice of prime matter, its transformation and the technique of fabrication are also depending on the state of society.

So, what archaeologists find, may generally be considered as a sampling of an historical production process. Mapping the diffusion of the product, finding its chronological limits, understanding its social use, are the ways to insert this artifact into history.

Then, the building of groups takes also quite a different character: instead of letting things blindly order by themselves, we start from artifacts homogeneous historically and build up a reference group. From there we may try to separate this group from others and to recognize its exported members.

Let us suppose we have found, at least some of those sites through a systematic survey. On each site, let us suppose again that we have been able to select the large

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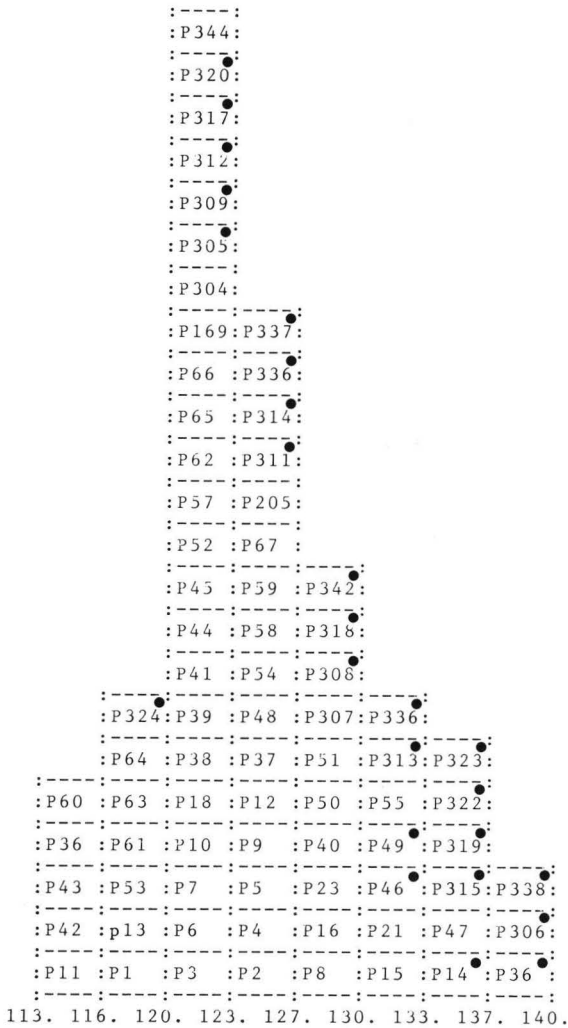


Fig. 1. Beaucaire amphorae workshop. Distribution of G4 amphorae edge diameters (DL in mm). From Laubenheimer (1983).

series of the type, we are trying to classify, rejecting what is not locally produced, and the local marginal types, the »five-legged sheep».

By taking measurements of dimensions on pots, we can obtain a set of parameters considered as random variables and try to classify those pots through multivariate statistical methods like cluster analysis (Fig. 1—3).

When such group appear, they will often characterize a production. Sometimes they will subdivide a workshop production, by hands of potters, or in time. The remarkable result is that selected shape parameters present a dispersion of relative ranges of the same order of magnitude as chemical parameters. So we will eventually be able to mix the two sets of parameters to help separating groups.

Is it useful to mention that precise measurements are necessary and that measures taken on photos or drawings give generally irrelevant results?

Then, last but not least, a careful observation of the technique used and of the ap-

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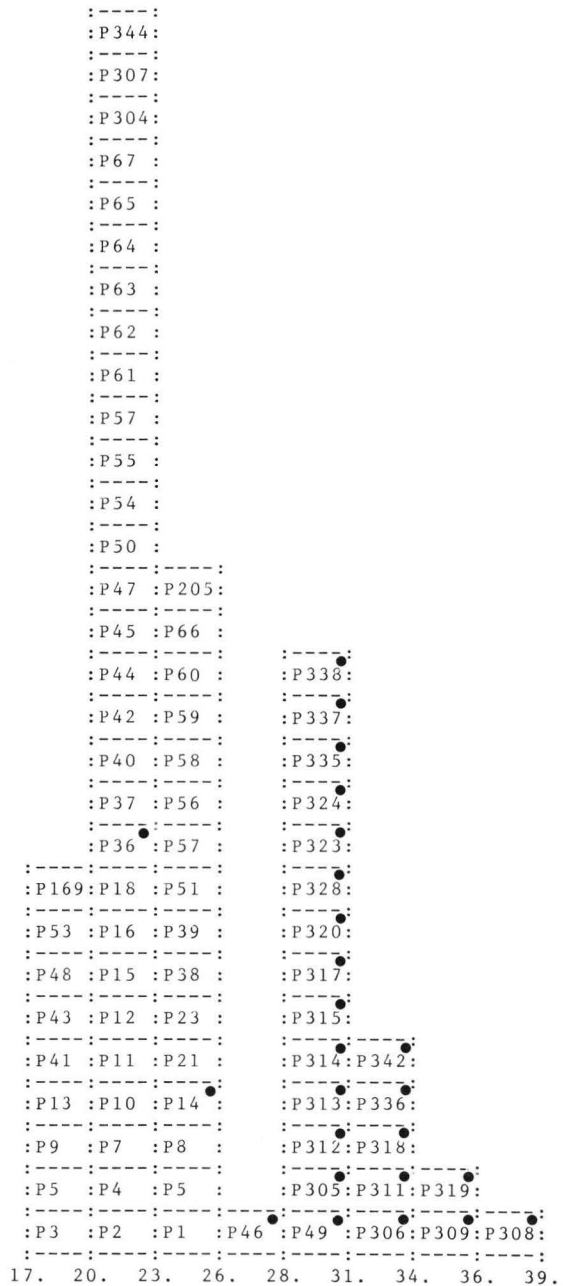


Fig. 2. Beaucaire amphorae workshop. Distribution of G4 amphorae edge thicknesses (EL in mm). From Laubenheimer (1983).

pearance of the baked clay can also bring an useful contribution to the characterization of the production. However, such descriptive approach can seldom be quantified, and easily enters the world of subjectivity. Colour of fabrics can be particularly variable within the same production, and misleading.

With all those informations why do we need analysis? In fact, even in a case we

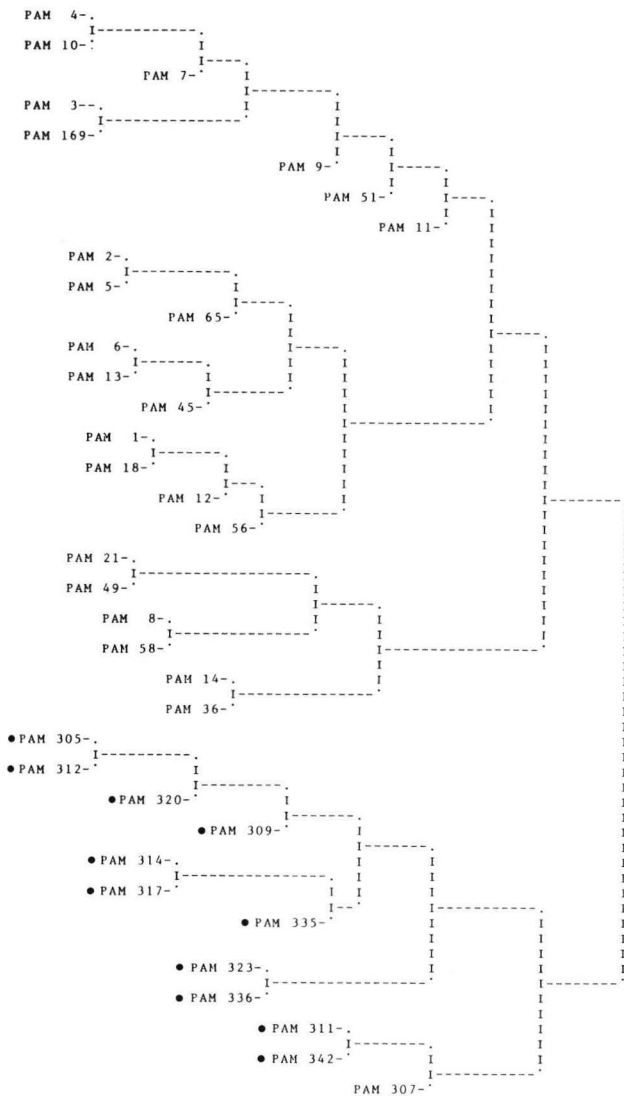


Fig. 3. Beaucaire amphorae workshop. Cluster analysis of G4 amphorae with 5 variables: height diameter, and thickness of the edge; width and thickness of the handle. The two groups appeared on the latter histograms — and not practically visible on the amphorae — are here well separated; • = group 2. Those groups are not yet interpreted. From F. Laubenheimer (1983).

studied in Orsay since several years, surveying more than fifty workshops having produced amphorae in Roman Gaul, only a few sites could be excavated and delivered a sampling suitable for statistical typology.

Fortunately, chemical analysis can work on small sherds. The idea of analyzing ceramics is by no way a new one. In the early nineteenth century the mineralogist Alexandre Brongniart (1770—1847) studied raw and baked clays properties, analysing them in the perspective of studying ancient techniques for application to the modern industries of bricks, tiles and ceramics. His »Traité des Arts Céramiques« issued in 1842 contains the first chemical analysis of ceramics as far as I know (Brongniart, 1842).

Twenty years later Ferdinand Fouqué (1828—1904) whose major contributions were in the very beginning of vulcanology, noticed during a stay in the Greek island of Santorini, some potteries, remains of the Minoan civilization, buried in volcanic ashes by the famous eruption occurred during the XIVth century BC.

He seems to be the first to have, through analysis of the pottery clays and comparison with the analysis of the local earth imagined the principle of characterization of origin through analysis (Fouqué, 1869).

Near the end of the century, T.W. Richards (Richards, 1895) noticed the similarity in the compositions of the groups of clay material: the necessity of very precise analysis is a consequence.

So, at the beginning of this century the formulation of the problem was already correct. But the analytical techniques reduced to wet chemistry were slow and tedious.

For lack of practical mean of analysis, the archaeologists of the first half of the XXth century, made groups out of ceramics through visual observation of clay fabrics, more or less sophisticated, from the simple fracture description to the thin section microscopic observation.

I will not insist on it, Dr. Birgitta Hulthen's lecture gave on this more light than I could do.

The observation of thin layers is indeed a very nice method provided one does not try to ask it more than it can do: there is no map of natural inclusions in clays and deducing an origin from the presence of certain minerals is risky. However, for the choice of samples and for the cross-cutting of analytical results with direct observation, it is a very important backing of analytical origin studies.

Back to the historical view of ceramics analysis, during the fifties, the first analytical studies using physico-chemical techniques appeared: X-ray fluorescence with curved crystal dispersion and Neutron Activation Analysis with sodium iodide detectors; they were, at the stage of technique, of a difficult use.

It is only near the beginning of the seventies, that decisive progress both in analytical techniques and in computers, allowed the issue of the first large studies of some types of ceramics, and of stone tools (for last review papers see Harbottle, 1982).

In those years, also the number of physico-chemical methods of analysis applied to archaeology increased: mass spectrometry, atomic absorption, charged particles activation analysis do not seem, however, suitable for ceramics analysis: mass spectrometry and atomic absorption require vaporization of the sample, made of numerous refractory oxides. The large variation of vaporization yield among chemical elements makes calibration a heavy job often done with the help of NAA.

Charged particles have a short range penetration in matter: some 100 microns, variable with energy of particles and cross-section of target material, so the analysed volume is very small. Recent results of analysis with PIXE on thick or thin ceramics targets have shown a great lack of reproductibility (L. Lessard, private communication; Brissaud et al.).

A problem of analysis of very small volumes is also coming from the limit of homogeneity of available standards, that requires a minimum mass. In practice, two analytical techniques led till now to the constitution of large data bases: XRF and NAA, the second being largely predominant in the number of samples stored.

Obvious advantages of NAA are the analysis in the whole volume of sample and the very high sensibility that allows the determination of more than 30 elements with a useful precision.

But a more fundamental reason has been emphasized elsewhere (Widemann, 1980). Practically, all analytical methods show an increasing difficulty for measuring elements with smaller and smaller abundance; so the choice of tracers will essentially be the major elements and possibly some »big traces» with an efficiency rapidly decreasing, as rapidly as the abundances themselves: typically, in the earth crust, the ratio is about 2.10^7 between the most abundant: silicon and the scarce gold. NAA has this unique

property of reproducing in a reactor the so-called r-process the predominant way heavy elements were constituted from light ones during the formation of the solar system (Trimble, 1975).

This basic fact has a very important consequence for the list of elements measurable from NAA: when an element had a small cross-section (σ) for neutron capture, it acted in the progressive nucleons agglutination as a bumper: it accumulated and eventually has a strong abundance, N . This is the case of silicon. On the contrary an atom of an element with a high cross-section had a tendency to disappear soon after its formation through a new cycle capture- β radioactivity: it remained scarce. The result is a rough tendential law that can be written:

$$N \times \sigma \sim \text{constant}$$

rather good for $A > 80$.

NAA is then the only exception among the analytical techniques where the maximum sensitivity of analysis is not for the most abundant elements. It allows the determination with the same order of precision of elements differing with several orders of magnitude of natural abundances without excessive intensity from the abundant elements.

For example tantalum, that in clay is about 10^{-6} and iron, about $3 \cdot 10^{-2}$ are measured with the same order of precision in the same counting. Being aware of the necessities for origin studies, we can examine the experimental conditions giving the best chances to answer the questions.

Experimental conditions must be examined along the whole chain: the choice of samples, the equipments, the way of using them and the data processing.

The choice of samples is most delicate. In origin studies occur two sorts of samples: the members of reference groups supposed to characterize an origin. One could better say to characterize not even a workshop but in general a certain group in the outputs of this workshop. For instance, the Roman factory of terra sigillata of Lezoux in Central France issued products with different compositions depending on time and on the sort of product.

Fig. 4 shows the separation of groups from the same workshop by neutron activation analysis. Two types of amphora and fine ware make three distinct groups. The Tressan G4 amphorae are closer to the composition of G4 from Aspiran than the fine ware of Aspiran. Then the technical difference is stronger than the distance (~ 10 km). This is only to insist on the representativity of the sampling. The latter example shows that a product from a workshop cannot always be taken as a reference of composition for another product. Local natural clays will of course present more varieties and even when used, differences from baked clays due to technical processes.

The close similarity of compositions makes an obligation of a careful hunting, of all sources of error, for example, variation in the shape of samples, or in the geometry of counting, or the smallest contamination before irradiation can introduce biases. Perfectionist maniacs are welcome for this kind of experiment. Germanium detectors of the best quality and sophisticated programmes removing any alien contribution from peaks used in gamma spectra are required: this would need alone long explanations I cannot give here.

Once numbers have been acquired, the data processing is the next step with criteria of attribution of an origin, to define for each kind of processing. Most treatments use reduced composition numbers as coordinate in the vectorial space of compositions.

A distance is defined in this space. It can be a simple Euclidian distance or something more sophisticated. Then, a common procedure is to build a dendrogramme with a

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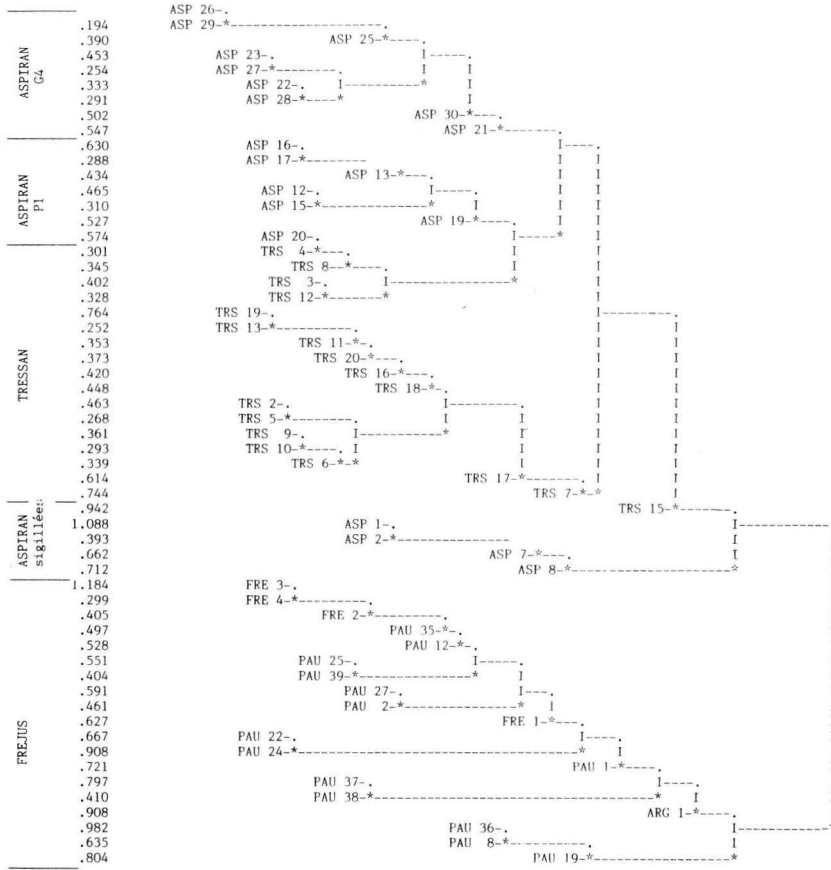


Fig. 4. Cluster analysis of NAA results on 18 chemical elements, on samples from three potters' workshops of Southern France: Aspiran, Tressan and Fréjus. The 3 categories of products from Aspiran form 3 groups. The Tressan neighbour workshop's amphorae are closer, in chemical composition, to the Aspiran amphorae than the Aspiran fine ware. It shows the limits of the help to be expected in origin studies from the side of geological and geochemical studies: our composition groups are production groups. The Fréjus group, from a remote workshop, is also much further away in composition. From Fontes et al. (1981).

programme of cluster analysis, just in the same way we have classified dimensions of ceramics; it is not my aim to describe here those very common classification techniques. I would make a remark: those system are grouping in a given collections the closest compositions: any way they will. They even will be able to build a group from data victim of a systematic experimental error, or out of sherds presenting an alteration from weathering (Rottländer, 1983).

Cluster analysis is only a system of ordering distances. Groups obtained from this method have to be taken only as tentative groups. Any sample will generally enter the group the closest. But by no way it gives an idea of the variations within a group or between a group and an exported sample the programme brings into.

We need calculating whether the variation of the groups are of an order usual in ceramics groups and when it is for exported material, whether the distance between the exported sample and the center of the group is short enough.

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 IST 4- I
 MBC 66-
 MBC 69-1
 MBC 64-1
 MBC 2-1
 MBC 63-1-
 MBC 68-1 I
 MBC 67- I
 MBC 16- I
 MBC 24-1 I
 MBC 10-1 I
 MBC 28-1 I
 MBC 37-1 I
 MBC 30- I
 MBC 15- I
 MBC 31-1 I
 MBC 62- I
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 OST 307- I
 OST 593- I
 OST 362-
 SAA 8-
 SAA 10-1
 SAA 1-
 SAA 2-
 SAA 9-
 SAA 6-1
 SAA 7- I
 SAA 5- I
 SAA 4- I
 SAA 19- I
 SAA 21- I
 SAA 18- I
 SAA 20- I
 OST 311- I
 OST 594-
 PAU 39-
 FRE 3-1
 FRE 4- I
 PAU 19- I
 PAU 25- I
 PAU 27- I
 PAU 2- I
 PAU 35- I
 PAU 8- I
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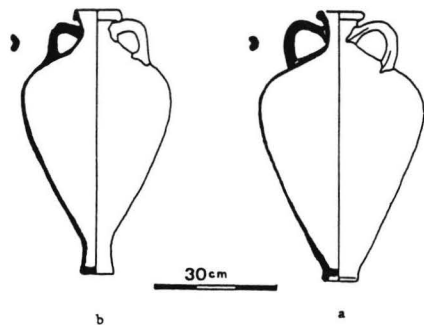


Fig. 5. Gauloise 4 and Dressel 30 amphorae similar shapes and cluster analysis of some workshop from Southern France and the Northern African stamped amphorae from Ostia. The latter form a very isolated group including the Saldae shard (OST 351) and several unstamped amphorae.

This calculation can be done in different ways. Perlman and Asaro, wrote a programme named GROUP, that gives this distance in term of probability of belonging to a given group. It is a programme very simple, using Euclidian distance only and showing clearly for each sample the contribution of each element to the probability. We use it as a very transparent test for fishing up last mistakes or acknowledge alterations. It allows to use a simple statistical criterium that allows to calculate how many elements will together deviate from the group mean, in the same sample by $0 \rightarrow 1\sigma$, $1 \rightarrow 2\sigma$, $2 \rightarrow 3\sigma$, as a function of the number of elements analysed (Widemann, et al., 1975).

So, the procedure we use is first cluster analysis to know where to begin groups. Then we use the GROUP program as a filter to check the dispersion of the proposed groups. Then after introducing the new group in the data bank we can check 1) if the new group is well distinct from the others, 2) if exported ceramics fit this new group.

We found for this last operation that discriminant analysis is often a better filter than the program GROUP. We have been using recently a programme called MAHAL 3 written by Romeder (1973) and adapted to our machine and our data by Naciri and Leblanc.

Finally, I would like to give a recent example of results obtained in Orsay by our group using the preceding method.

We have been classifying amphorae of Gallic shape found in Ostia by comparison of their chemical composition with the data base, we buildt on the workshops groups (23 groups now). Until the end of the IInd century A.D. it does not seem to be any doubt about the Gallic origin of those amphorae, even when they are not classified because of the lacunae of our data base (with the exception of a small group of possible northern Spain origin). But after the Severian era, North Africa started the production of an amphora type very similar to the most common Gallic type: G.4 (Widemann, et al., 1978).

We had in Ostia, among the supposed African amphorae imitated from G.4 ones, some bearing stamps giving the origin of the amphora: Tubusuctu, 25 km up the Soummam river in Algeria, plus one from Saldae (modern Bejaia).

We could obtain a reference group of a very narrow dispersion: 10.28 % of root mean square deviation over the 25 best elements measured. The Saldae sherd is in the middle (Fig. 5). The group is characterized in particular by a high content in iron: 4.79 % and elements linked with it: scandium, cobalt, chromium.

We can observe its good separation from the Gallic groups on cluster analysis confirmed by discriminant analysis, in this favourable case, almost unnecessary. We could use that good separation to exclude from this group three stamped amphorae, supposed to be from the same origin: CAS reverse, PATRICI and SEPTIM. On the contrary, three unstamped amphorae, of which classification was nothing but obvious, enter the group. We can therefore conclude with a good security that they came from the lower Soummam valley, most likely Tubusuctu.

This example shows the possibilities of this method in finding the precise origin of artefacts that could have come from an area a thousand kilometers away. Years of work were necessary to build up the data base. When it is done, the classification work is quick and secure.

REFERENCES

- Brissaud, I., Houdayer, C., Jehanno, C. and Sabir, A., 1985. Pottery analysis using PIXE, neutron activation, electron microscopy and X-ray fluorescence techniques. JRANC 89/2, 473—486.

- Brongniart, A., 1842. *Traité des arts céramiques*. Paris.
- Fontes, P., Laubenheimer, F., Leblanc, J., Bonnefoy, F., Gruel, K. and Widemann, F., 1981. Nouvelles données analytiques et typologiques sur les ateliers d'amphores en Gaule du Sud. *Revue d'archéométrie* 6, 29—38.
- Fouqué, F., 1869. Une Pompéi antéhistorique. *Revue des deux mondes* 83, p. 923.
- Harbottle, G., 1982. Chemical characterization in archaeology. In *Contexts for prehistoric exchange*. J.E. Ericson and T.K. Earle, ed. New York.
- Laubenheimer, F., 1983. La production des amphores en Gaule Narbonnaise sous le Haut-Empire. Thèse de doctorat d'Etat, U. de Montpellier. To be published.
- Richards, T.W., 1895. The composition of Athenian pottery. *Am. Chem. J.* 17, p. 152.
- Romedor, J.M., 1973. *Méthodes et programmes d'analyse discriminante*, Dunod, Paris.
- Rottlander, R., 1983. Poster session at the 1983 symposium on archaeometry, Naples.
- Trimble, V., 1975. The origin and abundances of the chemical elements. *Rev. of Mod. Phys.* 47, p. 877.
- Widemann, F., 1980. NAA for provenance studies of archaeological artifacts. *JRAC* 55, p. 271.
- Widemann, F., Picon, M., Asaro, F., Michel, H.V. and Perlman, I., 1975. A Lyons' branch of the pottery making firm of Ateius of Arezzo. *Archaeometry* 17, p. 45.
- Widemann, F., Laubenheimer, F., Attas, M., Fontes, P., Gruel, K., Leblanc, J. and Leres, J., 1978. Analytical and typological study of Gallo-Roman amphorae in the area of Narbonne. *Archaeophysika* 10, p. 317.