Three issues of the *MASCA Journal* will be published in 1985 including a special Supplement on archaeometallurgy.

Subscription rates for 1985 are:

U.S. $11.00 for 2 issues (excluding the Supplement),
U.S. $6.00 for the Supplement only,
U.S. $16.00 for all 3 issues.

Subscriptions should be prepaid and checks made out to *MASCA Journal*. Requests for Exchange subscriptions should be made to the Editors.

All enquiries, communications, manuscripts, and books for review should be sent to the Editors, *MASCA Journal*, Museum Applied Science Center for Archaeology (MASCA), The University Museum, University of Pennsylvania, 33rd and Spruce Streets, Philadelphia, PA 19104, U.S.A.

The contents of the articles in the *MASCA Journal* are solely the responsibility of the authors, and views expressed therein in no way reflect those of either the editors of the *Journal* or of the MASCA organization.

Plate 1, opposite: Overview of Sarepta excavations looking west towards the Mediterranean. A pile of crushed *M. trunculus* shells and purple-colored sherds were discovered in the vicinity of the pottery kiln in the foreground. (Photograph: Courtesy of J.B. Pritchard, The University Museum.)

ROYAL PURPLE AND THE PRE-PHOENICIAN DYE INDUSTRY OF LEBANON

P.E. McGOVERN R.H. MICHEL

MASCA The University Museum University of Pennsylvania Philadelphia PA 19104

Introduction

Purple dyes have probably been produced by chemical processing of the secretions of the hypobranchial glands of Mediterranean gastropod molluscs (*Murex brandaris, Murex trunculus,* and *Purpura haemastoma*) since the mid-second millennium B.C. (Fig. 1). Shell heaps on Crete and elsewhere in the Mediterranean (Reese 1979-80) and along the Levantine coast (*e.g.*, at Ras Shamra, Sidon, and Tyre) have provided the primary archaeological evidence for the industry, which is also attested to in Akkadian and Ugaritic texts from the Late Bronze Age (*e.g.*, Thureau-Dangin 1934; Schaeffer 1950). While the middens may be *prima facie* evidence for the industry, particularly if they are of one species, they could possibly represent a food source. The archaeological identification of an industrial complex and/or the chemical confirmation of the ancient dye would provide much less ambiguous evidence for the origins and development of the industry.

The Iron Age Phoenicians, whose name may even derive from a root meaning "purple" (Speiser 1936; Landsberger 1967), were acclaimed in the first millennium B.C. for fabrics dyed with Royal Purple (Bruin 1970). Such fabrics were widely traded in the Near East, and carried by the Phoenicians to all parts of the Mediterranean. The only extensively excavated Phoenician site in the homeland of Lebanon, Sarepta (Sarafand), produced an archaeological sequence extending back into the thirteenth century B.C. (Pritchard 1978; Khalifeh, in press; Anderson, in press) (Plate 1, facing page). In Strata III-IV of Area II-A-8, three sherds of a standard Late Bronze Age storage jar type were discovered, whose interiors were covered with a purple-colored accumulation. Several murex shells, primarily *M. trunculus* but also including one example of *M. brandaris*, were found in the same locus and in adjoining squares in the same stratum (Reese, forthcoming). Fragments

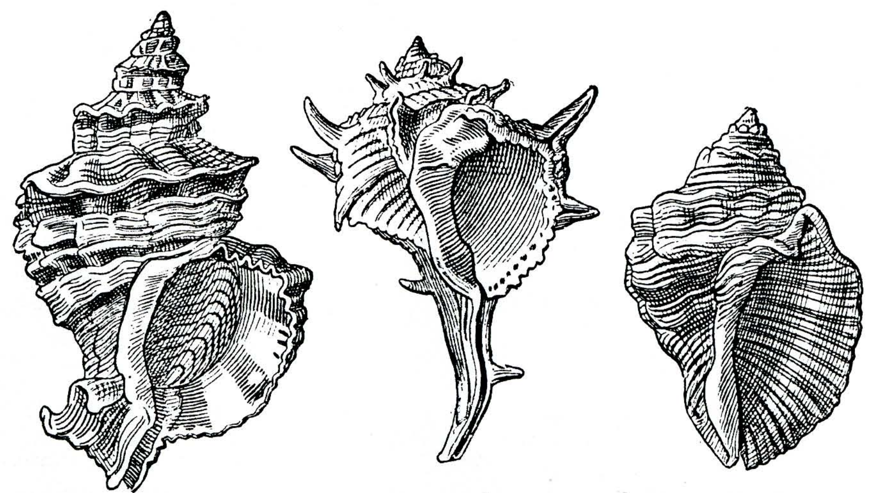


Fig. 1:
a., *M. trunculus*
b., *M. brandaris*
c., *P. haemastoma*
(After Besnier 1877-1919.)

of a spouted vat (Plate 2) with a purple sediment on its interior came from a square (II-B-6) 10 m north in a stratigraphically related context. In Area II-B-9, approximately 10 m to the southeast, three more such sherds of a pithos or krater type from the transitional Late Bronze-Early Iron Age (Stratum V), were recovered. Associated with the latter was a large pile of crushed *M. trunculus* in Area II-C-9.

The vat from II-B-6 is similar in shape to pot bellows from metallurgical installations (Davey 1979), but may well have had other industrial purposes. Some sort of pre-processing of the mollusc material would obviously be required to separate the dye-producing gland extracts from extraneous animal matter, perhaps according to methods described in much later writings (*e.g.*, Pliny the Elder). The spouted vat would be an ideal vessel to drain aqueous extract, while removing solid residues which floated on the surface.

The chemical composition of the dyes from the three Mediterranean molluscs has been previously investigated (Fouquet and Bielig 1971; Baker 1974; Ziderman 1981). *M. brandaris* and *P. haemastoma* yield mainly 6,6′-dibromoindigotin (X = Br in Structure 1 below), while *M. trunculus* gives the unbrominated indigotin (X = H) in addition to the dibromo compound. The proportions of the two dyes from *M. trunculus* can vary widely, depending upon how the mollusc extracts are processed. For example, prolonged exposure to air (oxidation) will leave primarily precursors for the dibromo compound in solution, whereas the major indigotin precursor is converted to the dye, which is insoluble and would probably be removed with the mollusc residues. Exposure of the remaining content of the solution to sunlight would then yield the dibromo compound, since about half of its precursor requires ultraviolet light to go to the insoluble dye. Consequently, the color of the dye derived from the *M. trunculus* can range between reddish purple (6,6′-dibromoindigotin) and bluish violet (indigotin).

Structure 1

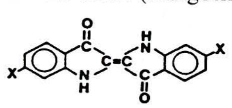


Plate 2:
Spouted vat containing purple sediment (Sar. no. *3237*).
(Photograph: Courtesy of J.B. Pritchard, The University Museum.)

Table 1: Electron spectroscopic chemical analysis of unknown and synthetic purples

Element	Binding energy (in eV)		Structural environment of the element
	Unknown purple	Synthetic 6,6′-dibromo-indigotin	
O	533	532	
N	401	400	unoxidized, as amide, amine, nitrite
Ca	350	349	
C	289	289	carbonyl, unresolved mixture
C	285	285	aliphatic, aromatic
Si	103	104	silicate type
Al	74.2	-	
Br	70.2	70.0	organic type

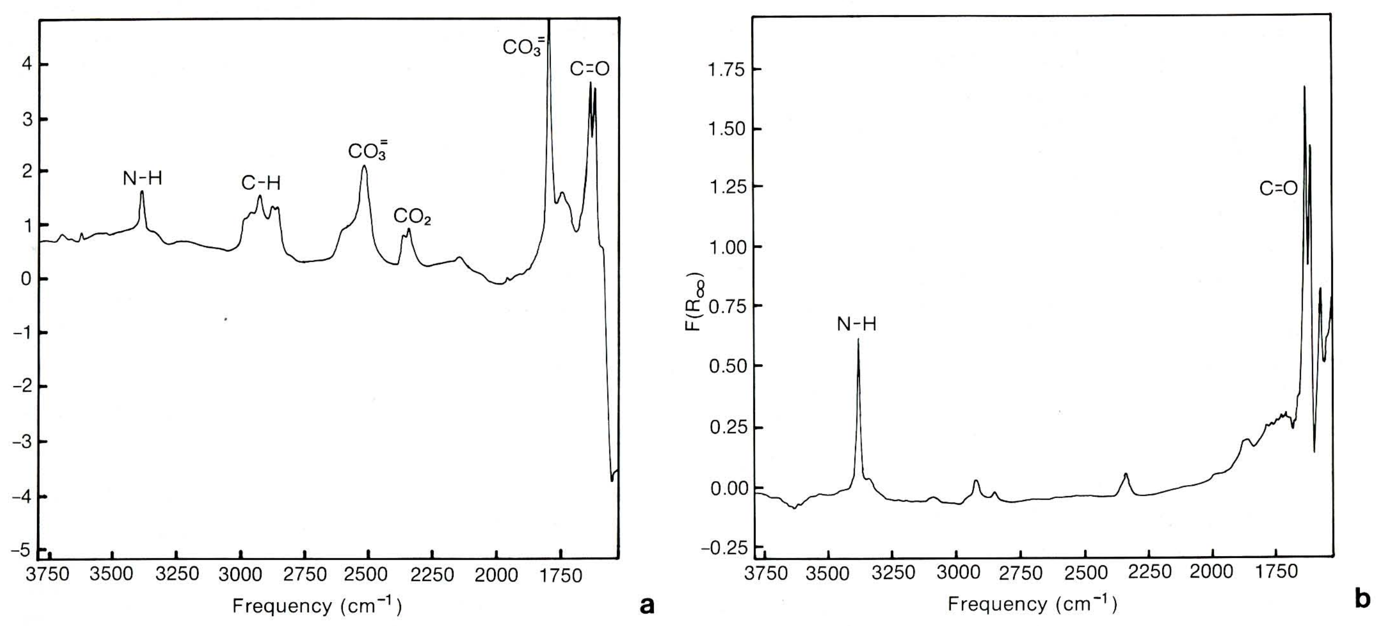
Spectroscopic investigations

All the Sarepta sherds were extremely small and had very thin accumulations of the purple material on their interior surface. A sherd from Area II-A-8, which measured about 5 cm square and whose purple coloration was relatively more intense than other examples, was chosen for the initial investigation. Because of the small sample, non-destructive spectroscopic techniques were first employed.

Proton-induced x-ray emission spectroscopy (PIXE) confirmed the presence of unusually high levels of bromine in the purple layer (0.322% versus 0.002% for the exterior surface lacking the color). Elements with atomic weights less than sodium, however, could not be detected by this method.

The specific chemical environment of the bromine was determined by electron spectroscopic chemical analysis (ESCA). As a reference for the unknown ancient specimen, a sample of synthetic 6,6′-dibromoindigotin, which had been deposited from a sodium hydrosulfite solution onto an uncoated Sarepta storage jar sherd from the same locus, was also tested. As can be seen from Table 1, the ancient purple is virtually identical to the 6,6′-dibromoindigotin. Specifically, the compound is attested to by the presence of unoxidized nitrogen, of carbonyl and hydrocarbon carbon, and of organic bromine. Other elements (Ca, Si, and Al) derive from the exposed pottery fabric.

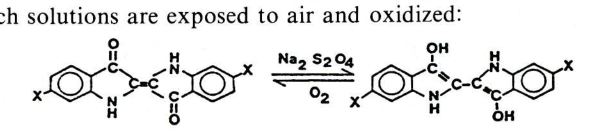
The presence of 6,6′-dibromoindigotin in the purple deposit was more definitely confirmed by diffuse reflectance Fourier transform infrared (FT-IR) spectroscopy. The spectrum of the ancient purple is compared with synthetic dibromoindigotin and indigotin deposits applied to ancient sherds from Sarepta (Fig. 2). The bromine substituent has a marked effect on the N-H absorption band, clearly differentiating indigotin (N-H at 3275 cm^{-1}) from 6,6′-dibromoindigotin (N-H at 3375 cm^{-1}). The N-H absorption band for unsubstituted indigotin is lacking for the ancient sample, which indicates that if such is present it



must be below the approximately 15% detection limit. The strong ceramic background accounts for the relatively low sensitivity in this region. The indigoid carbonyl band of the synthetic samples and ancient specimen is centered around 1625 cm^{-1}. It has the same shape and multiplicity in all the samples. The additional absorption bands for the ancient purple are from carbonate (probably as calcium carbonate), unidentified hydrocarbon(s), and carbon dioxide. The spectrum is limited to the region above 1500 cm^{-1} because of the ceramic background.

Chemical reactivity analysis

Conclusive evidence for the identification of the major dye component on the ancient sherd as 6,6′-dibromoindigotin came from an investigation of its chemical behavior employing semi-destructive methods. Indigoid materials are reduced by and dissolve in alkaline sodium hydrosulfite solutions to form the almost colorless leuco-base. They can be reprecipitated when such solutions are exposed to air and oxidized:



The reactions are characteristic of the vat dye family of which the two indigoids discussed here were the only known members in antiquity. Halogenated indigotins, such as 6,6′-dibromoindigotin, also dehalogenate to indigotin when their leuco-base solutions are exposed to ultraviolet radiation (sunlight, fluorescent light, *etc.*).

A sherd about 6 mm across was placed on filter paper on a hot plate and observed under low power magnification. It was heated to 60-80°C, when alkaline hydrosulfite solution at about the same temperature was dropped onto the surface at a rate that produced some overflow. When a change in the color intensity was observed, the filter paper was examined and found to have a small purple spot. As the filter paper remained

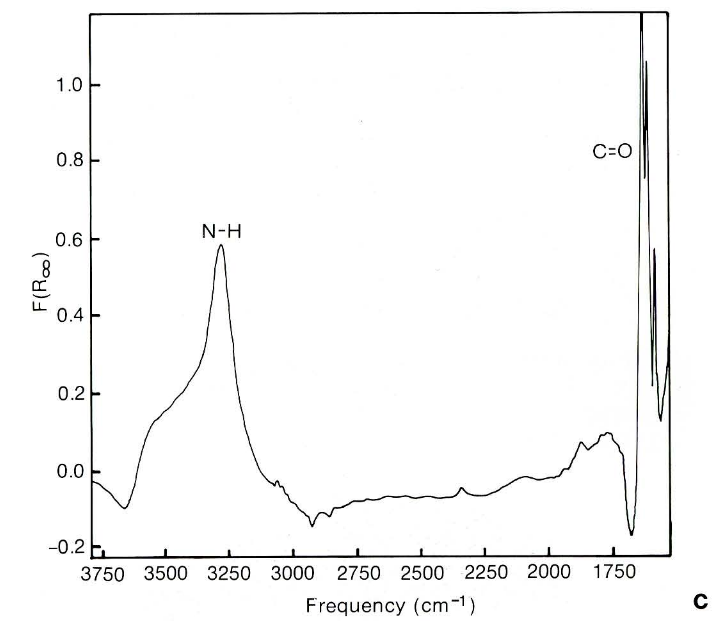


Fig. 2:
Infrared spectra of **a.**, unknown purple on Late Bronze Age sherd; **b.**, synthetic 6,6′-dibromoindigotin; **c.**, synthetic indigotin.

exposed to daylight and fluorescent light on the laboratory bench, the spot spread slightly and turned blue. The leuco-base of 6,6′-dibromoindigotin, which had not oxidized back to the dye, clearly had undergone photodebromination, followed by oxidation to the blue indigotin.

Conclusions

The combined evidence from the spectroscopic and chemical investigations leaves no doubt that the major component of the purple deposit on the Late Bronze Sarepta sherd is 6,6′-dibromoindigotin. *This is the earliest chemical confirmation of the ancient dye.* Its archaeological context points to local production of the dye rather than importation. The requisite mollusc species are represented in the loci with the purple-colored sherds, and a suitable industrial vessel, a spouted vat, came from an associated context.

What then was the mollusc source of the Royal Purple at Sarepta? *M. brandaris* yields a purple dye (6,6′-dibromoindigotin) exclusively. *M. trunculus*, when processed under reducing conditions as prescribed in modern and Graeco-Roman (Heinisch 1957) literature, will give about a fifty-fifty mixture of the unbrominated (blue) and brominated compounds. If *M. trunculus* had been used at Sarepta, one might therefore have expected to find blue or violet accretions on pottery. In fact, only purple-colored sherds were recovered.

Wider archaeological exposure would possibly resolve this problem by uncovering accumulations of *M. brandaris* shells in other contexts. However, it may simply be that the extracts from *M. trunculus* were exposed to air and oxidized. Then *most* of the precursors for indigotin would react to form insoluble dye, which might be entirely removed along with other solid residues. A large portion of the brominated precursors would remain in solution until converted to 6,6′-dibromoindigotin on exposure to sunlight. The end result would be a purple dye derived from *M. trunculus*. This points to an earlier experimental stage of dye processing, when the importance of a reducing environment and, by implication, of the vat method, was not well understood.

Acknowledgments

The generous contribution of services by E.I. DuPont de Nemours & Co. and its various spectroscopy laboratories in Wilmington, DE, is gratefully acknowledged. Very useful discussions regarding appropriate analytical techniques were held with S.C. Croft and E.G. Brame. R.C. Wendt and D.B. Chase are especially to be thanked for arranging to obtain the ESCA and IR data, and for helping to interpret the spectra. B.B. Baker and C.E. Day also offered valuable advice on interpreting the infrared spectra. The proton-induced x-ray emission spectroscopy (PIXE) was carried out in collaboration with C.P. Swann of the Bartol Research Foundation at the University of Delaware, Newark. Synthetic 6,6′-dibromoindigotin was kindly provided by S.M. Edelstein and D.H. Abrahams of Dexter Chemical Corp. A stimulating meeting with I.R. Ziderman clarified a number of points.

The study was first prompted by discussions with I. Khalifeh and J.B. Pritchard. The latter provided the ancient sherd and some of the natural dyestuff which had been extracted and processed from the three Mediterranean species by J.E. Doumet (nd). W.P. Anderson supplied additional samples, as well as detailed stratigraphic information from his dissertation (in press) and that of I. Khalifeh (in press).

Postscript

A purple accumulation has also been noted on the interior of a pithos from Tell Keisan, dated to the eleventh century B.C. (Puch 1980). Infrared analyses of purple-colored sherds from Shiqmona of 9th or early 8th century B.C. date by S.M. Edelstein have identified the purple as 6,6′-dibromoindigotin (personal communications from S.M. Edelstein and N. Karmon). Both sites are located south of Tyre along the Mediterranean coast in Israel, and were occupied by the Phoenicians in the Iron Age.

References

Anderson, W.P., in press: *Sarepta I: The Late Bronze and Iron Age Strata of Area II, Y.* Publications de l'Université Libanaise, Section des Études Archéologiques, vol. *1* (Librairie Orientale, Beirut).

Baker, J.T., 1974: *Endeavor 33*, 11.

Besnier, M., 1877-1919: in *Dictionnaire des antiquités grecques et romaines 4*, 770 (Eds. C. Daremberber and M.E. Saglio, Hachette, Paris).

Bruin, F., 1970: in *Sociétés et campagnies de commerce en Orient dans l'Océan Indien*, 73 (Bibliothèque Générale de l'Ecole Pratique des Hautes Étude, VI^e Section, S.E.V.P.E.N., Paris).

Davey, C.J., 1979: *Levant 11*, 101.

Doumet, J.E., nd: "Étude sur la couleur pourpre ancienne et tentative de reproduction du procédé de teinture de la ville de Tyr décrit par Pline l'Ancien" (Published by the author, Beirut).

Fouquet, H., Bielig, H.-J., 1971: *Angewandte Chemie* (Intern.) *10*, 816.

Heinisch, K.F., 1957: *Fibres (Engineering and Chemistry) 18*, 203.

Khalifeh, I.A., in press: *Sarepta II: The Late Bronze and Iron Age Periods of Area II, X.* Publications de l'Université Libanaise, Section des Études Archéologiques, vol. *2* (Librairie Orientale, Beirut).

Landsberger, B., 1967: *Journ. of Cuneiform Studies 21*, 139.

Puch, E., 1980: in *Tell Keisan (1971-1976): Une cité Phénicienne en Galilée*, 226 (Eds. J. Briend and J.-B. Humbert, Editions Universitaires, Fribourg).

Pritchard, J.B., 1978: *Recovering Sarepta, A Phoenician City* (Princeton University, Princeton).

Reese, D.S., 1979-80: *Libyan Studies 11*, 79.

Reese, D.S., forthcoming: "The Sarepta Shells."

Schaeffer, C.F.A., 1950: *Les Annales Archéologiques de Syrie 1*, 188.

Speiser, E.A., 1936: *Language 12*, 121.

Thureau-Dangin, F., 1934: *Syria 15*, 137.

Ziderman, I.I., 1981: *Journ. of the Society of Dyers and Colourists 97*, 362.