

**Figure 1.** Gastropod molluscs

Top, *Murex trunculus*; center, *Murex brandaris*; bottom, *Purpura haemastoma*  
(After Besnier, M. "Dictionnaire des antiquités grecques et romaines," Daremberg, C.; Saglio, M. E., Eds.; Hachette: Paris, 1877–1919; Vol. 4, p. 770.)

# PU

## Royal Purple Dye:

The Iron Age Phoenicians—whose name may derive from a root meaning “purple”—were acclaimed in the first millennium B.C. for fabrics dyed with Royal Purple—6,6'-dibromoindigotin. Such fabrics were widely traded in the Near East and carried by the Phoenicians to all parts of the Mediterranean. The dye continued to be produced in later periods, when it became equivalent to its weight in gold. Thus, Cleopatra's boat displayed a purple sail at the Battle of Actium in the first century B.C., and Nero issued an edict in the first century A.D. making the dye the preroga-

# The Analytical Approach

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# ROYAL PURPLE

## Tracing Chemical Origins of the Industry

tive of the emperor. Detailed descriptions of the dye industry can be found in the writings of Pliny the Elder, Strabo, and Plutarch, among others. Its importance to the clergy, continuing to the present day, can be traced back to the Israelite High Priest who had specific garments dyed with the purple.

Archeologists have long known from ancient writings that purple dyes were produced by extraction of the secretions of the hypobranchial glands of Mediterranean gastropod molluscs (*Murex brandaris*, *Murex trunculus*, and *Purpura haemastoma*) (Figure 1) since the early first millennium B.C. Shell heaps on Crete and elsewhere in the Mediterranean and along the Levantine coast (e.g., at Ras Shamra, Sidon, and Tyre) have provided the primary archeological evidence for the

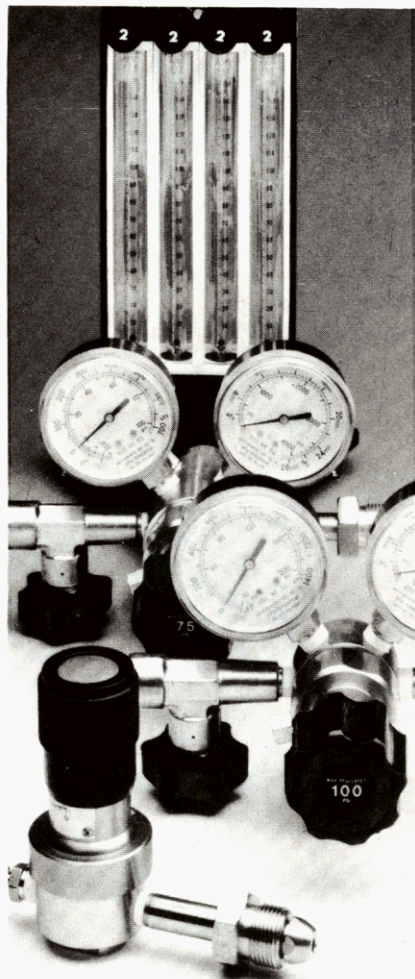
industry, which is also referred to in Akkadian and Ugaritic texts from the Late Bronze Age. Although these mid-den deposits may be prima facie evidence for the industry, particularly if the shells are of one species, they could also represent a food or lime source. The archeological identification of an industrial complex or the chemical confirmation of the ancient dye would be much less ambiguous evidence for the origins and development of the industry.

Therefore, when pottery sherds with purple deposits (Figure 2) were discovered at Sarepta (modern-day Sarafand), the most extensively excavated Phoenician site in Lebanon, they immediately attracted attention as possibly being related to the famous dye. They were recovered from an industrial complex with a large pile of

crushed shells nearby, primarily *Murex trunculus*, which dated to the thirteenth century B.C., or the end of the Late Bronze Age. If the purple were indeed Royal Purple, it would represent the earliest definitive evidence for the production of the dye, predating the Phoenician industry by several hundred years. Furthermore, the purple covered the inside of storage jars and unusual spouted vats, which might have been used to store and process the dye.

### Chemical background

The chemical composition of the secretions of the three Mediterranean molluscs, the dyes formed from them, and the process by which these conversions occur have been largely elucidated. The dye precursors are all sulfate esters of substituted indoxyls and



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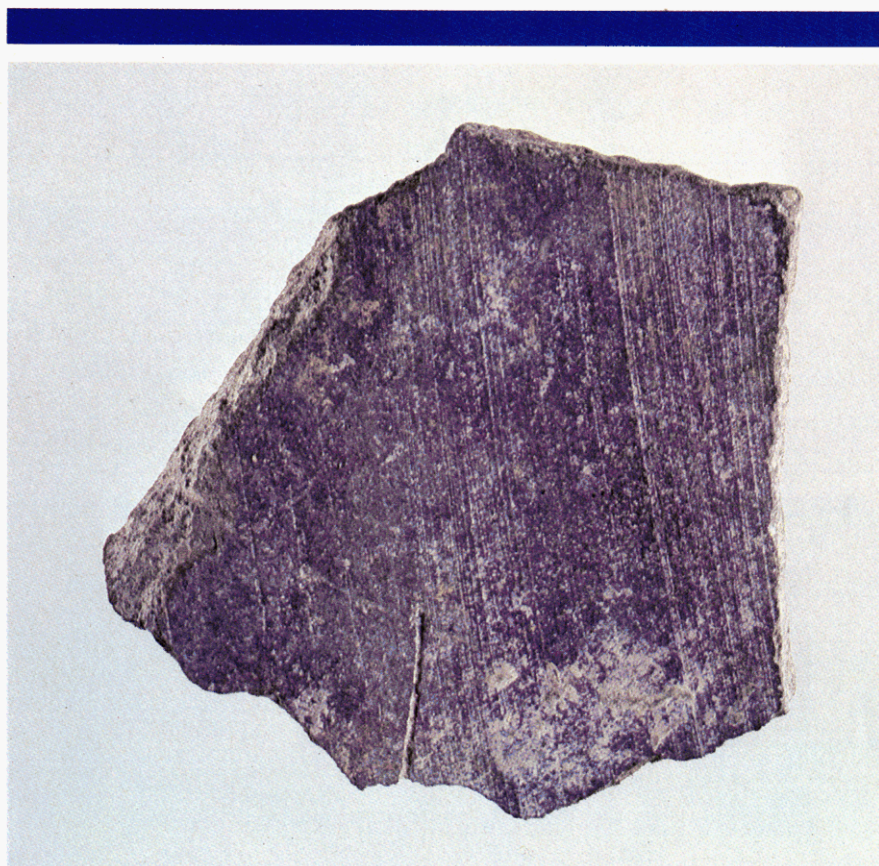
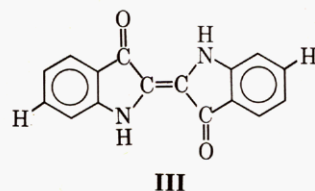
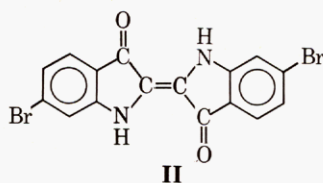
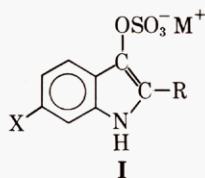


Figure 2. Sarepta sherd with purple deposit

of indoxyl itself (Structure I). They are converted to indigoid dyes by enzymatic hydrolysis of the sulfate ester, followed by oxidative (air) and photo-oxidative processes. *Murex brandaris* and *Purpura haemastoma* yield mainly the 6,6'-dibromoindigotin (Structure II), whereas *Murex trunculus* gives both the brominated and the unbrominated indigotin (Structure III).



Initially, fiber dyeing was probably carried out by direct application of a

relatively fresh extract of mollusc. When reducing systems were introduced, the precursor could be preserved as water-soluble indoxyl derivatives, or the dye itself, once formed, could be redissolved as the leuco base. The chemistry of the latter process is essentially identical to the ancient vat dyeing process used for natural indigo. At what point in time and in what form reducing systems came into use with mollusc-derived dyes have not yet been established.

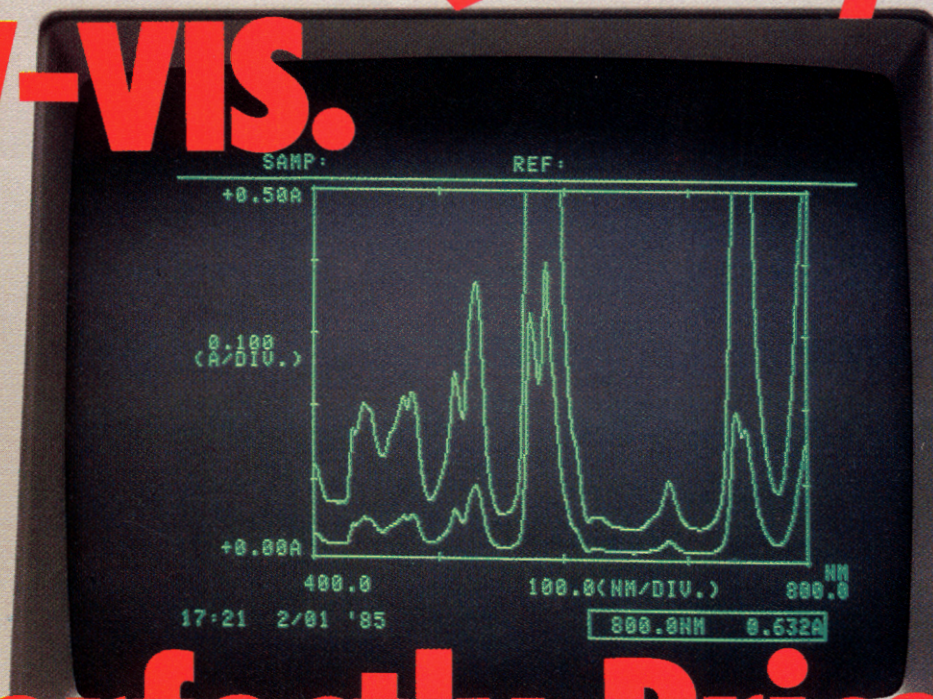
#### Sherd analysis

All the Sarepta sherds were extremely small and had very thin accumulations of the purple material on their interior surfaces. A sherd which measured ~5 cm square and whose purple coloration was relatively more intense than the other examples was chosen for the initial investigation. Because of the small sample, nondestructive spectroscopic techniques (proton-induced X-ray emission spectroscopy [PIXE], electron spectroscopic chemical analysis [ESCA], and diffuse-reflectance Fourier transform IR spectroscopy [FTIR]) were first used. After the spectroscopic data had been evaluated, chemical reactivity tests were carried out. Only a square centimeter of the sherd was required for all of the analytical work.

The analysis by PIXE was carried out by a two-step process. First, a

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**Table I. Electron spectroscopic chemical analysis of unknown and synthetic purples**

Element	Binding energy (eV)		Structural environment of the element
	Unknown purple	Synthetic 6,6'-dibromoindigotin	
O	533	532	
N	401	400	Unoxidized, as amide, amine, nitrile
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

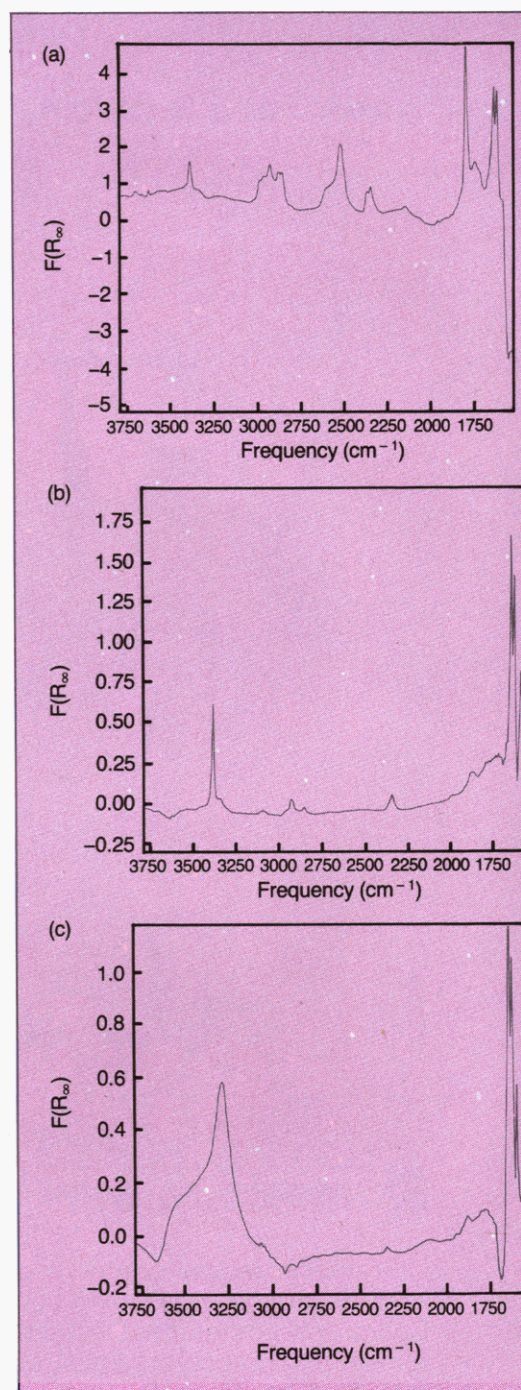
1.3-MeV proton beam, which was generated by a Van de Graaf accelerator, was directed onto the sample in a helium atmosphere to measure the low-atomic-weight elements. Then, 2.0-MeV protons were beamed onto the sample in an air or nitrogen atmosphere, with potassium chloride, vanadium, and aluminum filters to block out lower energy X-ray interference. Typically, 25 elements were measured. The results of the PIXE analysis of the purple deposit showed the presence of unusually high levels of bromine (0.322% vs. 0.002% for the exterior surface lacking the color). Elements with atomic weights less than sodium, however, could not be detected by this method, nor could information regarding the specific chemical environment of the bromine be obtained.

This additional information was provided by 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 (leuco base solution) onto an uncoated Sarepta storage jar sherd from the same locus and of the same date, was also tested. The analyses, carried out with a Du Pont 650 electron spectrometer, demonstrated that the bromine was bonded to the carbon with the same binding energy (70.2 eV) as the bromine in the synthetic 6,6'-dibromoindigotin reference sample. ESCA analyzes only to a depth of about 50 Å, and thus only the upper part of a deposit, which is many times thicker, is examined. Because the surface is subject to environmental contamination and the exudation of substances from the interior, the ESCA analysis may not be completely representative of the bulk of the purple deposit. With this proviso, it will be noted in Table I that all the necessary elements for dibromoindigotin are present (neutral nitrogen, carbonyl and hydrocarbon carbons, organic bromine), in addition to the several elements that comprise

clay or the soil of the region (silicon, aluminum, and calcium).

The presence of 6,6'-dibromoindigotin as a major component of the purple deposit is most strongly supported by its diffuse-reflectance IR spectrum (FTIR). Figure 3 shows the spectra of the ancient purple accumulation and synthetic 6,6'-dibromoindigotin and indigotin applied to a comparable ancient sherd from leuco base solutions. They were obtained using a Nicolet 7199 spectrometer and a diffuse-reflectance bench; spectral subtraction by a computer algorithm was used to reduce the inorganic background. Figure 4 is the diffuse-reflectance spectra of powder mixtures of the synthetic dyes and KBr. A comparison of these sets shows that there are no shifts in absorption bands due to interaction with the ceramic, nor are there any changes resulting from the application of a synthetic dye from sodium hydrosulfite solution. The bromine substituent has a marked effect on the N-H band and clearly differentiates indigotin (NH at 3275 cm<sup>-1</sup>) from 6,6'-dibromoindigotin (NH at 3375 cm<sup>-1</sup>). The ancient purple's NH band is that of the dibromo derivative. There is no significant evidence for the unsubstituted indigotin, but in view of the large background subtraction (the ceramic contributed a broad hydroxyl band in this region), small amounts (15%) of indigotin would be difficult to detect. The indigoid carbonyl band of all the reference samples and of the ancient purple is centered about 1625 cm<sup>-1</sup>, and it has the same shape and intensity in each sample. At wavelengths below 1500 cm<sup>-1</sup> the background from the sherds was so intense that no meaningful spectra of this region could be obtained.

The ancient purple spectrum has at least four additional regions of absorption. The 2350 cm<sup>-1</sup> band is due to CO<sub>2</sub> from a small imbalance in the spectrometer's reference and sample beams. The 2500 cm<sup>-1</sup> and 1800 cm<sup>-1</sup>

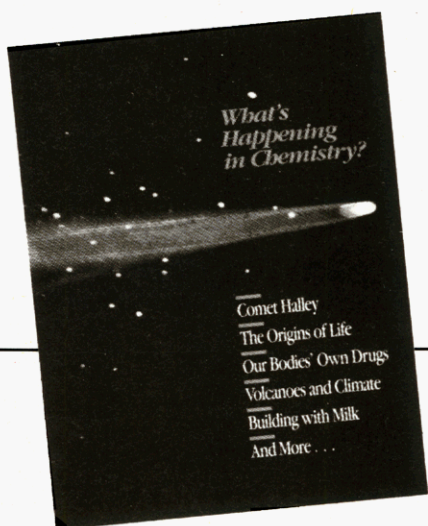


**Figure 3. FTIR spectra of dye deposits on Late Bronze Age ceramics**

(a) unknown purple, (b) synthetic 6,6'-dibromoindigotin, and (c) synthetic indigotin

bands are from carbonate ion, probably in the form of calcium carbonate that was added intentionally as a temper or was deposited by groundwater. CH bands at 2900–2850 cm<sup>-1</sup> could be organic residues from the processed mollusc, or they could be more recent contaminants. An exact determination is impossible without additional information regarding the structure of these CH-containing materials.

The final and conclusive evidence for the identity of the major dye component is derived from its chemical



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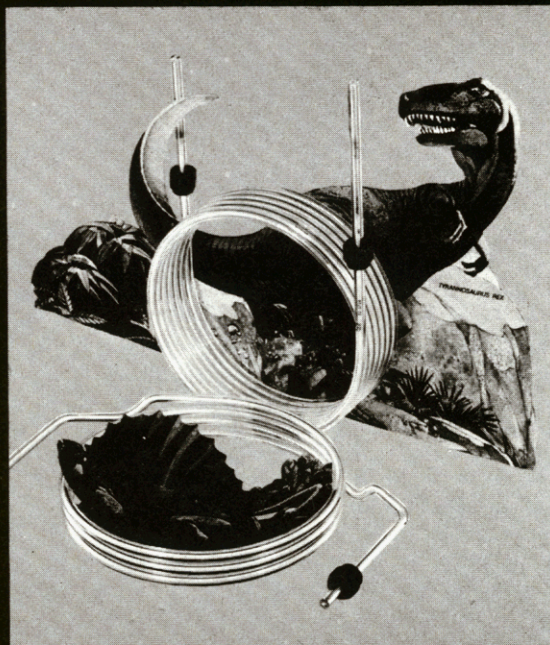
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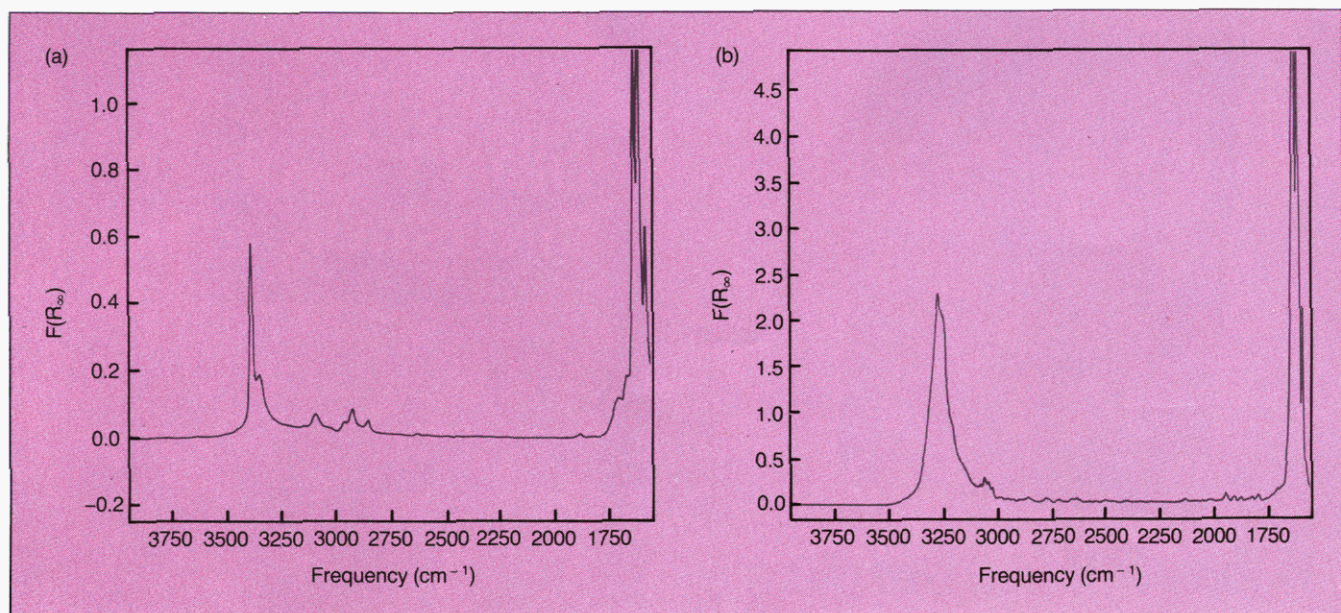
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**Figure 4.** FTIR spectra of dyes on KBr powder  
(a) synthetic 6,6'-dibromoindigotin and (b) synthetic indigotin


behavior. Indigoid materials dissolve in alkaline sodium hydrosulfite solution as the almost colorless leuco base and are reprecipitated when such solutions are exposed to air (oxygen). The chemistry of the leuco base reactions is:



The reactions are characteristic of the vat dye family of which indigotin and 6,6'-dibromoindigotin were the only known members in antiquity.

The halogenated indigoids, such as 6,6'-dibromoindigotin, dehalogenate to indigotin when their leuco base solutions are exposed to UV radiation (daylight and fluorescent light). In the case of the above compound, this dehalogenation is accompanied by a color change in the oxidized form from purple to blue.

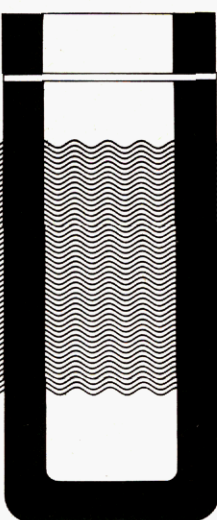
A sherd ~6 mm in diameter with purple deposit was placed on filter paper on a hot plate and observed under low-power magnification. It was heated to 60–80 °C, and alkaline hydrosulfite solution at about the same temperature was dropped onto the purple surface at a rate that produced some overflow. When a change in the color intensity was observed, the filter paper directly under the sherd was examined and found to have a small purple spot. As the filter paper remained exposed to daylight and fluorescent light on the laboratory bench, the spot spread slightly and turned blue. Leuco base of 6,6'-dibromoindigotin, which had not yet oxidized back to the dye, had undergone photodebromination, which is characteristic of halogenated indigoids. The chemical behavior of the deposit confirms the conclusions drawn from the IR spectra that the



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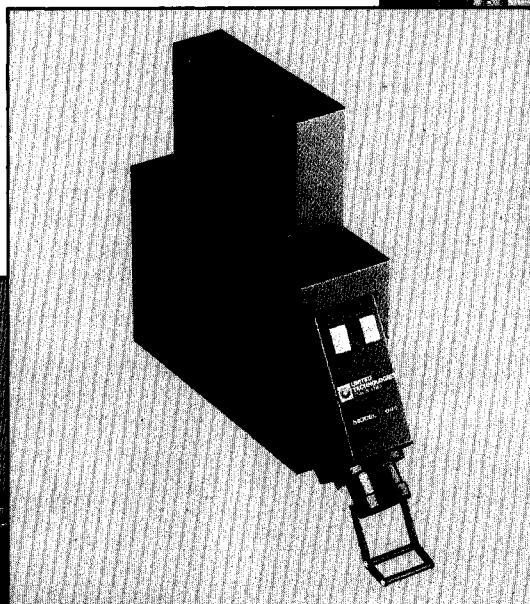
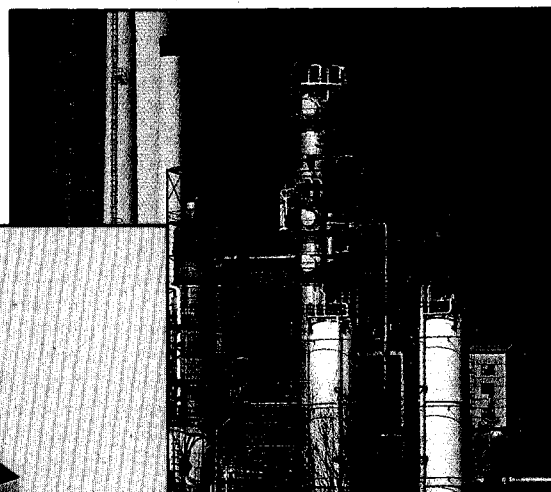
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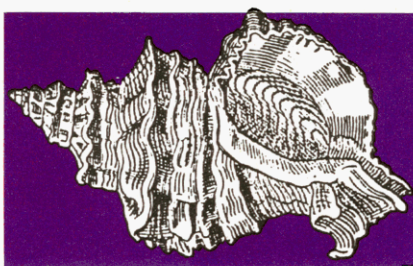


major dye component must be 6,6'-dibromoindigotin.

### Mollusc source

What then was the mollusc source of the Royal Purple at Sarepta? Almost all of the associated mollusc shells were of the *trunculus* species, which would normally be expected to produce a mixture of about equal amounts of 6,6'-dibromoindigotin (purple) and indigotin (blue), yielding a violet coloration. The chemical analyses of the purple accumulation on the ancient sherd, however, showed no admixture of the unbrominated compound with 6,6'-dibromoindigotin. The *brandaris* species yields a purple dye (6,6'-dibromoindigotin) exclusively, but only one unbroken shell of this kind has been excavated at Sarepta to date.

In fact, the composition and color of the end product from the *trunculus* species are very dependent on how the extracted secretions are processed. As one hypothetical scenario, if the extract were not kept in a reducing environment and were exposed to air during prolonged processing, about 90% of the precursors forming blue indigotin would be converted to the dye prematurely. The dye is insoluble and would probably be removed with other



mollusc residues. The remaining solution would then yield primarily 6,6'-dibromoindigotin on exposure to sunlight. This may point to an earlier stage of dye processing when the importance of a reducing environment for retaining the soluble indoxyl precursors (and by implication, for vat dyeing) was not understood.

Because the sherds with the purple accumulations are from the thirteenth century B.C., this is the *earliest* chemical confirmation of the ancient dye. As such, it bears significantly on the early development of the industry that was to become a symbol of Phoenician expertise and commerce. The archeological evidence points to local production of the dye rather than importation. The requisite mollusc species are represented in the areas with the purple-colored sherds, and a suitable in-

dustrial vessel, a spouted vat, came from an associated context. The combined evidence leaves little doubt that a dye factory was fully operational at Sarepta toward the end of the Late Bronze Age.

### Acknowledgment

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