Purple Dye

Different shades of purple dye on silk.
Photo Tony Farraj.

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Ancient Purple Dyeing by Extraction of the Colour from *Murex Phylonnus Tronculus, Murex Phylonnus Brandaris, Thais Purpura Haemastoma* and Whelk Following the *Natural History* of Plinius Secundus Caius called Pliny the Elder (23 AD – 79 AD)

This article is based on an earlier study (Joseph Doumet, A Study on the Ancient Purple Colour, Beirut, Imprimerie Catholique, 1980). It is written in tribute to Pliny the Elder whose *Natural History* describes the dyeing technique used in Tyre using sea gastropods (Books IX, XXXI, and XXXIV). In the previous study, which relied heavily on the description in Book IX, many lacunae and inconsistencies in Book IX prompted further independent research to reconstruct the process. This article describes how a further reading of Books XXXI and XXXIV confirms that sea gastropods of the Murex family were used in antiquity to dye wool (then a key textile) purple

Excavations covering the period until the first millennium BC revealed piles of *Murex phy. Tronculus* and Whelk shells. However, from the first millennium BC onward important piles of shells of mixed Murex used for dyeing were found in both southern Italy and in the towns of Tyre and Sidon (Phoenicia). These piles consisted of shells of *Murex phy. Tronculus*, Whelk, *Murex phy. Brandaris* and *Thais Purpura Haemastoma*, in different ratios in each pile.

When *Murex phy. Tronculus* and its variant the Whelk are crushed and macerated in fresh or sea water, they begin to tint the liquid purple after approximately one or two hours. This is independent of the composition of the vessel used (metal, ceramic). After two to three days, an intense violet-red liquid is obtained. This liquid, cannot be used for dyeing. Two or three hours later wool is steeped in it (meaning before the full precipitation of the dye) for a period of two to three days (complete precipitation of the dye). After washing this wool will have acquired a relatively deep purple colour. Repetition of this process intensifies the colour. The remaining coloured liquid can no longer be used for dyeing. We can conclude that the gastropods *Murex phy. Tronculus* and Whelk crushed and mixed with water release a substance; this substance by reaction with environmental chemical agents produces a purple precipitate. This process was used before the first millennium BC to dye wool in a variety of vessels using only *Murex phy. Tronculus* and Whelk and before the dye precipitated completely. The same result cannot be obtained by this method using *Murex phy. Brandaris* and *Thais Purpura Heamastoma* alone. Experiments carried out with these two species were negative. The fact that archaeologists found piles of mixed shells of the four species dating from after the first millennium BC leads us to suppose an evolution in the art of purple dyeing involving the use of the four species. Our source of documentation is the *Natural History* of Pliny the Elder. Book IX describes the process to be followed, which, however, when applied literally, does not yield results. More information can be found in Books XXXI and XXXIV, which fills in the gaps in the description in Book IX and is in accordance with the modern science of dyeing.

The Pliny description of the process in Book IX is the following:

(from Plinius Secundus Caius, *Natural History*, trans. H. Rackham, 1967-1975, 10 vols., The Loeb Classical Library, Harvard University Press, Cambridge, Mass.).

"It is most profitable for them to be taken after the rising of the dog-star or before spring-time, since when they have waxed themselves over with slime, they have their juices fluid. But this fact is not known to the dyers' factories, although it is of primary importance. Subsequently the vein of which we spoke

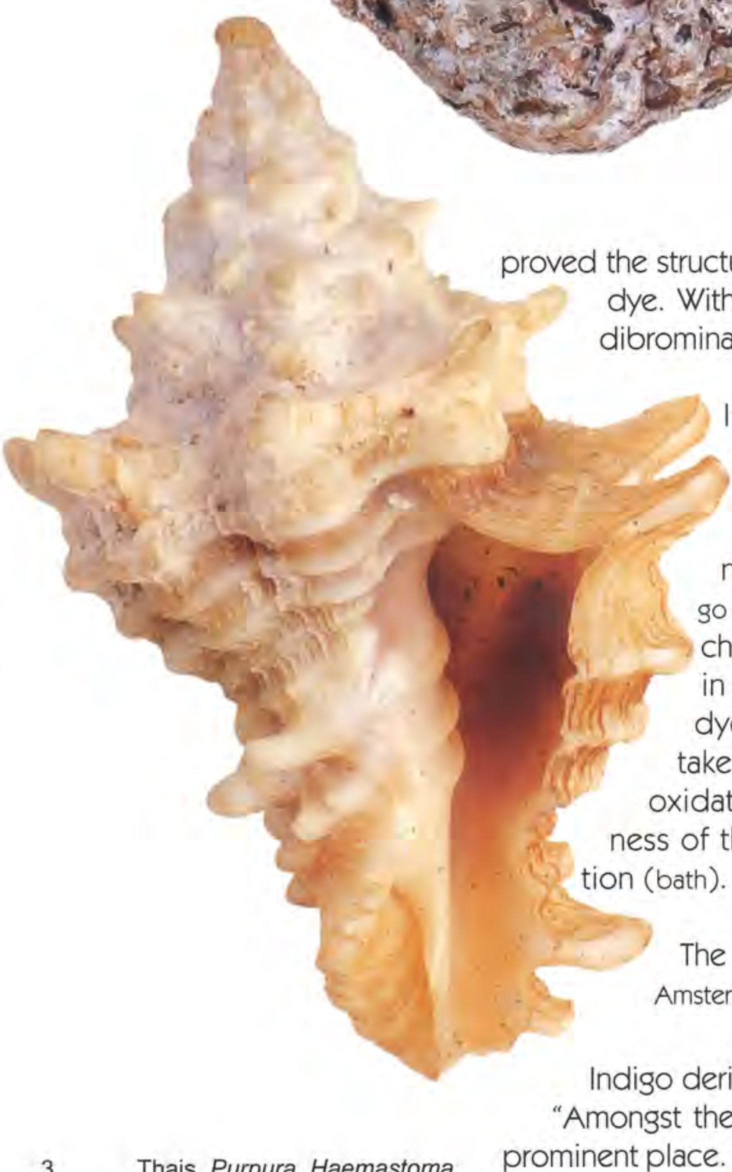
2 The product of the precipitated bath.

is removed, and to this salt has to be added, about a pint for every hundred pounds. Three days is the proper time for it to be steeped (as the fresher the salt the stronger it is), and it should be heated in a leaden pot, and with 50 lbs. of dye to every six gallons of water kept at a uniform and moderate temperature by a pipe brought from a furnace some way off. This will cause it gradually to deposit the portions of flesh which are bound to have adhered to the veins, and after about nine days the cauldron is strained and a fleece that has been washed clean is dipped for a trial, and the liquid is heated up until fair confidence is achieved. A ruddy colour is inferior to a blackish one. The fleece is allowed to soak for five hours and after it has been carded is dipped again, until it soaks up all the juice. The Whelk by itself is not approved of, as it does not make a fast dye; it is blended in a moderate degree with sea-purple and it gives to its excessively dark hue that hard and brilliant scarlet which is in demand; when their forces are thus mingled, the one is enlivened, or deadened as the case may be, by the other. The total amount of dye-stuffs required for 1,000 lbs. of fleece is 200 lbs. of Whelk and 111 lbs. of sea-purple; so is produced that remarkable amethyst colour. For Tyrian purple the wool is first soaked with sea-purple for a preliminary pale dressing, and then completely transformed with Whelk dye. Its highest glory consists in the colour of congealed blood, blackish at first glance but gleaming when held up to the light; this is the origin of Homer's phrase, 'blood of purple hue'".

It is not in fact possible to dye in purple with this description. It seems that Pliny wrote about a different procedure than the one which was described for wool dyeing before the first millennium BC. It is not possible either to leave the shells soaking for three days in a pure lead vessel with salt or to concentrate the liquid over a period of ten days without precipitating the dye.

Modern dyeing methods





3 Thais *Purpura Haemastoma* and *Murex Phylonnus Tronculus.*

The following is taken from R. E. Kirk and D. F. Othmer eds., 1947-1960 *Encyclopedia of Chemical Technology*, New York, volume I, p. 627:

"Tyrian Purple (CI Natural Vat Dye; 75800). On the shores of the Mediterranean in the ancient city of Tyre, there flourished a dyestuff industry as early as 3000-2000 BC. Hundreds of thousands of molluscs were processed there in order to obtain a purple dye, named Tyrian Purple after the city where it was produced. The mollusc commonly used was the *Murex Brandaris*, although other species were also known to produce a similar dye. The dye itself is not found as such in the mollusc but is formed by exposing to sunlight a pus-like secretion produced by the mollusc. Nothing, at present, is known as to the nature of the dye precursor.

It is related that the Romans paid as high as $150/lb for wool dyed with Tyrian purple. In fact, cloth so dyed was so expensive that only kings and priests could afford it. The term "born to the purple" is used even today to denote people of wealth or position. Although the colouring matter was investigated as early as 1873, it was not until 1909 that Friedlander proved the structure of the dye. From 12,000 molluscs, he obtained 1.4 g. of dye. With this material, he was able to show that Tyrian Purple is a dibrominated indigo (ie. 6.6' – dibromoindigo)".

In the twentieth century an artificial indigo dye was produced (this dye had previously been made from plants). The colour that indigo dye gives is blue; it is easy to brominate indigo and reproduce the purple colour artificially, namely the 6-6' dibromoindigo. These modern dyes (indigo and others produced from indigo) are vat dyes and used in a chemically reduced solution (leuco-form) that can be dissolved in alkaline solutions. The textile to be dyed is dipped in the dyeing solution for a fixed time (Pliny mentions five hours), then taken, wrung and exposed to air. The dye precipitates by oxidation in the textile fibers and colours the textile. The deepness of the colour corresponds to the concentration of the solution (bath).

The following is taken from P. Karrer, 1938, *Organic Chemistry* Amsterdam, p. 527-528:

Indigo derivatives. Indigoids.

"Amongst the simpler indigo derivatives the halogenated indigos take a prominent place. They are distinguished by great fastness to chlorine, and give brilliant shades. The shade of the dye varies with the number and position of the chlorine atoms which enter the molecule. Bromination of indigo in nitrobenzene gives successively the 5:5'-the 7:7'-, and finally the 4:'- derivatives:

Ciba blue B is 5:7:5'- tribromoindigo, ciba blue 2B is 5:5':7:7'- tetrabromoindigo, ciba blue G, or indigo MLB 5B consist of a mixture of tetra - and pentabromoindigo.

Hexabromoindigo and chlorinated indigos are also commercial products. 6;6' dibromoindigo deserves special mention. It has been shown by Friedlander to be identical with the pigment of the purple snail (*Murex Brandaris*) known as Purple of the Ancients: 1.5 gm. of dye is obtained from 12000 purple snails. It was formerly used as a purple dye, but is now no longer employed for this purpose. Substitution of bromine in the indigo molecule in the 6:6' positions clearly causes a displacement of the shade of the dye towards the red.

The principle of vat-dyeing is to reduce the insoluble dye to a phenolic derivative, the so-called leuco-compound, which is soluble in alkali. This is almost always lighter in colour than the dye, in fact, usually colourless. The thread is dipped in the alkaline solution and suspension of the reduction product, the "vat", is then exposed to the air. The oxygen oxidizes the leuco-compound on the fabric to the dye, and this is attached firmly to the cotton, apparently by absorption forces in the finely divided form in which it is produced. The use of vat-dyeing is obviously limited to those dyes which can be easily reduced, and of which the leuco-compounds can be readily re-oxidized to the original dye. Indigo shows this behaviour remarkably well. On reduction it takes up two hydrogen atoms and is converted into indigo-white, a substance which crystallizes in colourless leaflets. Atmosphere oxygen reconverts it quantitatively into the dye".

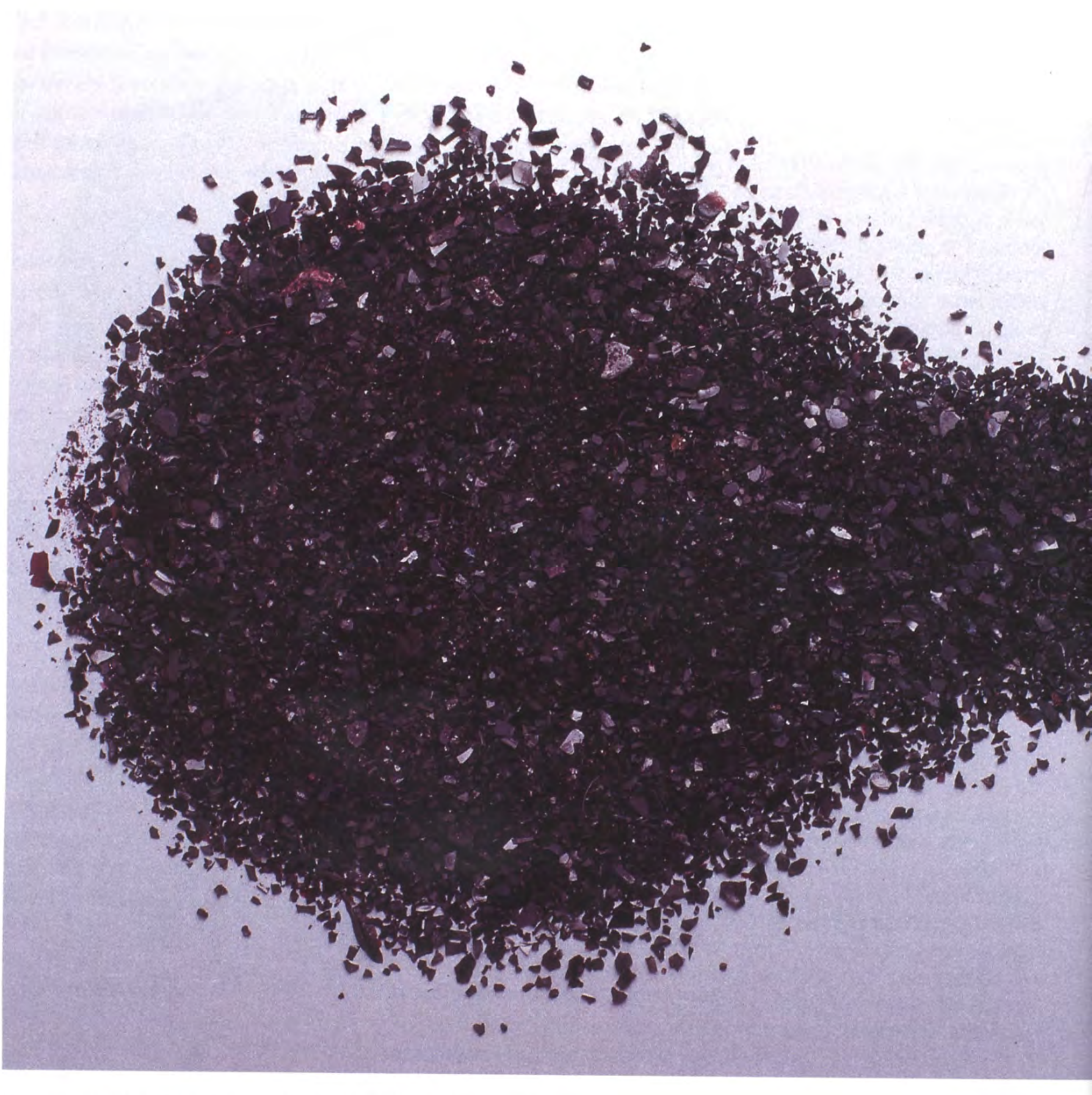
Dyeing trials with *Murex phy. Tronculus* and Whelk show that they release their dye in a chemically reduced colourless leuco-form; oxygen from the air precipitates the colour by oxidation. The product secreted by the *Murex phy. Tronculus* and by the Whelk can be dissolved in an alkaline bath (Karrer, 1938, p. 527). To avoid precipitation the ancients would have had to use an alkali soluble in water, and also a chemical reducer to stop the dye's precipitation. Had a soluble alkali and a reducer been known during Pliny's time, the method provided in Book IX would have been successful.

Supplementary information provided by Pliny in his *Natural History*

Pliny provides the following information in Book IX:

a It is necessary to add salt to the solution.
b The solution is heated in lead containers; the shells are soaked for three days; then the bath is concentrated.
c The concentration by evaporation is done at a moderate temperature. This necessitated the use of ends of chimney pipes. The concentration takes about nine days.
d Lead pots had to be used.

In order to follow Pliny's recipe a soluble alkali had to exist (salt is not an alkali) as well as a reducer. Salty solutions do not attack lead chemically so do not produce a reducing gas, and Pliny does not mention a chemical reducer to bring back a precipitated solution to the leuco-form.



4 The precipitated product reduced to a leuco-form by sodium ditionite and then further precipitated with acetic acid after filtering or centrifugation.

In Book XXXI Pliny writes:

"I must not put off describing the character of soda, which is very similar to salt" (p. 106).

The soda needed for the dye is soda ash (sodium carbonate, Na_2CO_3) but the salt in Pliny's recipe in Book IX is sodium chloride ($NaCl$). Pliny tells us that the salt from the sea is very slightly different from soda ash. In Pliny's time, the difference between sodium chloride and soda (an alkali) could hardly have been known, and Pliny could just as easily have said that soda should be added rather than salt.

Pliny's confusion is shown in Book XXXI:

"The former indeed think that the wood used also makes a difference. The best is oak, for its pure ash by itself has the properties of salt; in some places hazel finds favour. So when brine is poured on it even wood turns into salt. Whenever wood is used in its making salt is dark. I find in Theophrastus that the Umbrians were wont to boil down in water the ash of reeds and rushes, until only a very little liquid remained" (p. 83).

"But soda from burnt oak-wood was never made in large quantities, and the method has long been altogether abandoned" (p. 107).

"This soda is natural, but in Egypt it is made artificially, in much greater abundance but of inferior quality, for it is dark and stony. It is made in almost the same manner as is salt, except that they pour seawater into the salt-beds but the Nile into the soda-beds" (p. 109).

"Of soda the best is the finest, and therefore froth of soda is superior, for colouring purple cloths and all kinds of dyeing. Soda is of great use in the making of glass, as will be described in its proper place. The soda beds of Egypt used to be confined to the regions around Naucratis and Memphis, the beds around Memphis being inferior" (p. 111).

The following is taken from "Commentaires", *Histoire naturelle* de Pline l'Ancien, collection des Universités de France, Paris:

"Over Momemphis there are two pools very rich in soda. The town of Momenphis could have been situated on the occident side of the Delta between Memphis and Alexandria".

The alkali needed to dissolve the dye in leuco-form is specified by Pliny as Egyptian soda (sodium carbonate, Na_2CO_3) from "Naucratis" and the alkaline solution produced by washing wood ash. Wood ash contains potassium carbonate (K_2CO_3). The alkaline solution produced by washing wood ash can easily reach a pH of 12, and it is perfect for use in purple dyeing. It could have been used from the beginning of the first millennium BC. This is the alkali needed in Pliny's method in Book IX.

Returning to the chemical reducer needed to maintain the solution in leuco-form, we need to know whether lead can be attacked by alkaline solutions with a release of nascent hydrogen gas as a chemical deoxidizer (Karrer, 1938, p. 527–28). Modern chemistry informs us that lead is not attacked by alkali (soda) or by salt ($NaCl$) (*Metals Handbook, American Society for Metals*, Cleveland, Ohio, 1948, p. 960).

In Book XXXIV Pliny speaks about lead:

"The next topic is the nature of lead, of which there are two kinds, black and white. White lead (tin) is the most valuable; the Greeks applied to it the name cassiteros, and there was a legendary story of their going to islands of the Atlantic Ocean to fetch it and importing it in plaited vessels made of osiers and covered with stitched hides. It is now known that it is a product of Lusitania and Gallaecia found in the surface stata of the ground which is sandy and of a black colour. It is only detected by its weight, and also tiny pebbles of it occasionally appear, especially in dry beds of torrents. The miners wash this sand and heat the deposit in furnaces. It is also found in the goldmines

called Alutiae, through which a stream of water is passed that washes out black pebbles of tin mottled with small white spots, and of the same weight as gold, and consequently they remain with the gold in the bowls in which it is collected, and afterwards are separated in the furnaces, and fused and melted into white lead" (p. 156–8).

In the commentaries to Book XXXIV we learn the following:

"The plumbum Nigrum is lead and tin was the plumbum album or candidum" (p.156).

In Pliny the Elder's time tin was called white lead; it is just as likely that in his description of the dyeing process in Book IX, he could have written "white lead pots" as the phrase he did use, "lead pots". Is tin chemically attacked by alkalis causing the release of nascent hydrogen? This could solve the need for a reducer and could make it possible for the dyeing solution to stay in leuco-form.

In *Metals Handbook* (p. 1072) we find that tin is indeed chemically attacked by sodium or potassium hydroxides, but only slightly and persistently attacked by sodium and potassium carbonate (soda from Egypt or potassium carbonate solution produced by washing wood ash). The attack by sodium or potassium carbonate is slow and a continuous production of nascent hydrogen gas occurs. This being an excellent reducing agent, it allows the process described by Pliny in Book IX to succeed.

Successful experiments undertaken by the author in 1980 used not only soda ash but also a solution produced by wood ash leach in tin containers. *Murex Phy. Tronculus* and Whelk crushed in an alkaline solution held in a tin container do not show any colour after three days. This solution when decanted and used for dyeing stays practically colourless in a tin container. When textiles, wool staples, natural silk or cotton are taken out of the bath after dipping and wrung, they begin to colour in contact with the oxygen in the air, reaching a shade dictated by the bath's concentration; this solution can be completely exhausted of its dye. The same experiment in the same conditions, but tried with *Murex phy. Brandaris* and or *Thais Purpura Haemastoma*, failed.

French biologist R. Dubois, 1909 (*Archéologie Zoologique*, Dijon, p. 499), insisted on an enzymatic action for the formation of purple dye. As the *Murex phy. Tronculus* and the Whelk produce the purple colour, it was thought that these two species could possibly contain the enzyme mentioned by Dubois (Doumet 1980). Experiments using *Murex Phy. Brandaris* and *Thais Purpura Haemastoma* with only 10 per cent of *Murex phy. Tronculus* or Whelk in tin containers produced a dyeing bath with the four species mixed together. This explains the findings of piles of mixed shells of the four species in excavations at Tyre and Sidon.

In Book IX Pliny describes the concentrations of the solution at moderate temperature, kept at 35-40° celsius for nine days (Doumet 1980). This time gives the enzyme the opportunity to act. The recent discovery of the enzyme is explained in R. Jannun and E. Coe, "Biochemistry of Tyrian Purple Synthesis. II.

Murex Bromoperoxidase Activity" and E. Coe, R. Jannun, W. S. Ward, C. Chen, and J. Doumet, Biochemistry Department, American University of Beirut, "Biochemistry of Tyrian Purple Synthesis: Bromoperoxidase and Purpurase Activities of Murex. E.i", papers presented to *The 7th Science Meeting of the Lebanese Association for the Advancement of Science* (*LAAS*) with the support of the CNRS, Beirut, Lebanon, 8-11 April 1981.

"Murex sea snails have been known for their production of the dye "Tyrian Purple" since ancient times. Intermediates are known to include a bromoindoxyl sulfate derivate which dimerizes after hydrolysis by an aryl sulfatase (purpurase). Bromoperoxidase activity has now been identified in extracts of the dye-producing gland of *Murex Trunculus*. Generation of Br_2 from Br in the presence of H_2O_2 is detected by conversion of cresol red to bromocresol purple. Activity is localized in the particulate fraction but is solubilized in 1% Triton X-100 and differs from bacterial chloroperoxidase in its high pH optimum (8) and its low activity with Cl. Aryl sulfatase activity, which is present in the soluble fraction of the gland extract, shows a KM of 10-4 M with P-nitrophenyl sulfate at pH 7.5 and is competitively inhibited by phosphate. Its high pH optimum distinguishes it from the digestive aryl sulfatase of other mollusc".

The importance of tin in ancient purple dyeing industry

Using soluble alkali in tin containers could have been known at Tyre as early as the first millennium BC.

Letter of Hiram, King of Tyre to Solomon:
"Now, I have sent a skilled man, endued with understanding, Huram Abi, the son of a woman of the daughter of Dan, and his father was a man of Tyre. He is trained to work in gold, silver, bronze, iron, stone and wood and in purple, blue and crimson fabrics and fine linen" (II *Chronicles* 2:13–15).
From the description of Solomon's temple:
"And he made the veil of blue and purple and crimson fabrics and fine linen, and worked cherubin on it" (II *Chronicles* 3:14).
To perform purple dyeing in different tones, the bath had to be concentrated. It is astonishing that archaeological excavations, having found dyeing workshops, have never yet found tin containers. Tin was precious because of its use in the production of bronze.
In Book XXXIV Pliny tells us that tinning was known; so tinned containers could have been used for dyeing baths.
"When copper vessels are coated with stagnum the contents have a more agreeable taste and the formation of destructive verdigris is prevented, and, what is remarkable, the weight is not increased" (160).
"A method discovered in the Gallic provinces is to plate bronze (copper) articles with white lead so as to make them almost indistinguishable from silver; articles thus treated are called incoctilia" (162–3).
Tinning was also known long before the Roman period. Tinned articles were found while excavating near Alesia in Gaul. There is no evidence that people of the first millennium BC did not know the art of tinning copper. They were known as the best metallurgists of their time. Thus the ambiguities in Pliny Book IX about purple dye are resolved.

Pliny's identification of the Murex species, Book IX: 125, 128, 130, 131,132.

Purple *Phylonnus Brandaris* and Whelk (trumpet-shells)

"Purples live seven years at most. They stay in hiding like the murex for 30 days at the time of the rising of the dog-star. They collect into shoals in spring time, and their rubbing together causes them to discharge a sort of waxy viscous slime" (p.125).

"The purple's tongue is an inch long; when feeding it uses it for piercing a hole in other kinds of shell fish, so hard is its point. These fish die in fresh water and wherever a river discharges into the sea, but otherwise when caught they live as much as seven weeks on their own slime. All shell fish grow with extreme rapidity, especially the purple-fish; they reach their full size in a year".

The *Murex Phylonnus Brandaris* live covered by bottom sea sand and in spring time can only be found bound together for reproduction. At this moment it is easy to catch them (p. 128).

"Shell fish supplying purple and scarlet dyes – the material of these is the same but is differently blended – are of two kinds: the Whelk (trumpet shell) is a smaller shell resembling the one that gives out the sound of a trumpet, hence the reason for its name, by means of the round mouth incised in its edge; the other is called the purple, with a channelled beak jutting out and the side of the channel tube shaped inwards, through which the tongue can shoot out; moreover it is prickly all round, with about seven spikes forming a ring, which are not found in the Whelk, though both shells have as many rings as they are years old. The trumpet shell clings only to rocks and can be gathered round crags" (p. 130).

It is important to notice that Pliny mentions the *Murex Phylonnus Brandaris* with the Whelk (trumpet shell). *Murex Phylonnus Brandaris* does not produce purple dye but the Whelk does as it contains the enzyme. Therefore while dyeing in purple using the specie *Phylonnus Brandaris*, the Whelk is needed to introduce the enzyme in the dyeing bath.

Murex Phylonnus Tronculus

Pliny writes about the *Murex Phylonnus Tronculus*. Book IX.

"The murex also does this in a similar manner, but it has the famous flower of purple, sought after for dyeing robes, in the middle of its throat: here is a white vein of very scanty fluid from which that precious dye, suffused with a dark rose colour, is drained, but the rest of the body produces nothing. People strive to catch this fish alive, because it discharges this juice with its life; and from the larger purples they get the juice by stripping off the shell, but they crush the smaller ones alive with the shell, as that is the only way to make them disgorge the juice. The best Asiatic purple is at Tyre" (p. 125).

"The pebble-purple is named after a pebble in the sea, and is remarkably suitable for purple dyes" (p. 131).

Thais Purpura Haemastoma

About the *Thais Purpura Haemastoma* Pliny writes:

"A better kind is the reef-purple, collected on the reefs of the sea, though this also is lighter and softer as well" (p. 131).

For purple dyeing, *Thais Purpura Haemastoma* cannot be used alone; it has to be mixed with Whelk and or Murex *Phylonnus Tronculus*; both of these two species contain the necessary enzyme for purple dyeing.

It is difficult to provide from Pliny a clearer identification of the four species of gastropod used for purple dyeing. In Pliny's *Natural History*, in addition to Book IX, which describes the dyeing process with certain inconsistencies, Book XXXI mentions salt and soda, showing that an alkali existed that dissolved the dye. In Book XXXIV we discover that Pliny distinguished between white lead (tin) and lead. White lead producing nascent hydrogen leaves the solution in reduced leuco-form. The information missing from Book IX is thus found elsewhere and allows us to reconfirm all our previous assumptions.