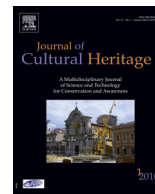




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Original article

# First evidence of purple pigment production and dyeing in southern Arabia (Sumhuram, Sultanate of Oman) revealed by mass spectrometric and chromatographic techniques



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## ABSTRACT

Archaeological excavations carried out in the ancient settlement of Sumhuram (3rd century BC–5th century AD) in the area of Khor Rori (Dhofar Governorate, southern Oman), brought to light pottery showing a pink-violet substance. In order to reveal the nature of this pink-violet colour, the substance was chemically examined by laser desorption-ionization mass spectrometry (LDI-MS) and high performance liquid chromatography–diode array detection (HPLC-DAD). The analytical investigations provided a detailed molecular composition of the organic fraction of the pink-violet material, highlighting the presence of 6,6'-dibromoindigo, 6-monobromoindigo, 6,6'-dibromoindirubin, 6- and 6'-monobromoindirubin, indigo and indirubin. The results revealed that shellfish purple was the source. In addition, in some of the pottery fragments, alizarin and purpurin, which are the molecular markers of madder type dyestuffs, were also ascertained by LDI-MS. The analytical results enabled us to draw hypotheses not only on the possible function of such vessels as dye baths, but also that, since Sumhuram was one of the most important harbours in southern Arabia during the pre-Islamic time, it was also possibly a centre for the production and trade of purple pigments.

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## 1. Introduction and research aims

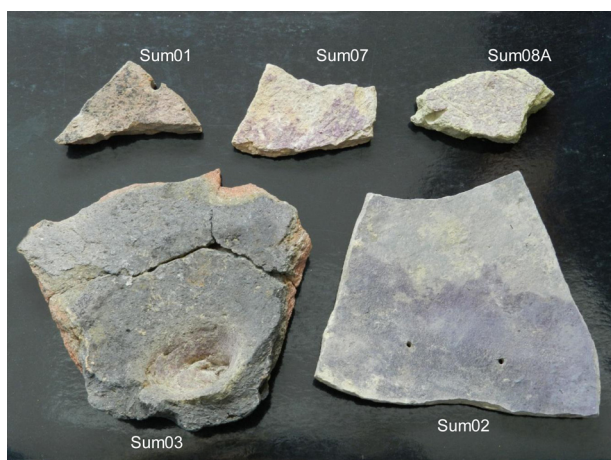
Since 1997, the Italian Mission to Oman (IMTO), directed by Prof. Alessandra Avanzini (University of Pisa), has been working in Sumhuram (southern Oman). Archaeological excavations have revealed a large number of findings that have proven to be excellent in terms of highlighting the activities of people living in a pre-Islamic city along the coasts of Arabia. Of the huge amount of archaeological materials recovered in Sumhuram, we focus here on a number of pottery fragments, all showing residues that consist of a pink-violet substance (Fig. 1).

Colorants and pigments have always been materials of great interest to understand ancient raw materials, trade routes and to open a window to the technological, scientific, and artistic developments of ancient people. For all these reasons,

an analytical approach entailing the use of laser desorption-ionization mass spectrometry (LDI-MS) and high performance liquid chromatography–diode array detection (HPLC-DAD) was used to reveal the origin of the coloured residues found in the ceramics. HPLC is the method of choice for analysing dyes [1], as most of the chromophores are polar compounds with a low volatility. It also enables a reliable quantitation of the detected analytes to be carried out. Laser-based ionization techniques have been proved to be valuable in studying organic pigments by mass spectrometric analyses [2–7]. The method requires minimal sample preparation, without any preliminary extraction. LDI-MS reveals the analytical information from a microscopic sub-sample with a minimum risk to the integrity of the original sample and within a very short time.

The ancient settlement of Sumhuram is located in the area of Khor Rori, in the region of Dhofar, southern Oman. Located along the coast, its natural harbour offers easy docking, and fresh water is available locally. Sumhuram was thus the ideal location for a busy and wealthy town along the route between the Mediterranean and

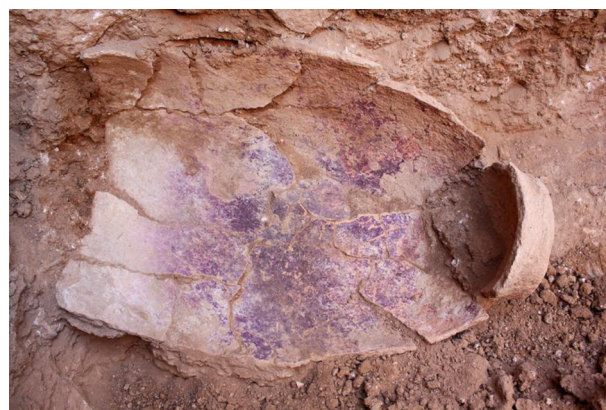
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**Fig. 1.** Some of the ceramic fragments found in Sumhuram, showing residues of pink-violet substances.

India (Fig. 2a). In fact, Sumhuram was a key site in the Indian Ocean commercial network in which it was involved since its early stages (3rd–2nd centuries BC), before the development of the lucrative Indo-Roman trade of the first centuries AD. Sumhuram is a small settlement (around 8000 m<sup>2</sup>), with many monuments, impressive city walls and monumental gate (Fig. 2b). The city has several quarters, with some areas devoted to productive activities and big open squares. Considered for a long time as just a commercial outpost, the site of Sumhuram was in fact an active settlement where many productive activities were carried on [8–10].

The shards found in Sumhuram belong to large storage or transportation vessels (amphorae and jars) sometimes with traces of burning attributed to a secondary use of the vessels. The overall shape of the containers was reconstructed from the fragments, but in some cases, it was not possible to attribute the shards to specific types because they were mostly fragments. An extraordinary discovery, however, was made in January 2015, when an archeologically complete open-mouth jar, standing on a ring base, was discovered (Fig. 3). The jar belongs to a well-known type of deep container, produced in southern Arabia, made from a coarse and porous ware where the main temper was straw. The porosity of the ware was, in this case, of great help in the conservation of the colorant, which had been absorbed by the walls of the container.



**Fig. 3.** The open-mouth jar, archeologically complete, recovered in Sumhuram (IMTO archive).

## 2. Materials and methods

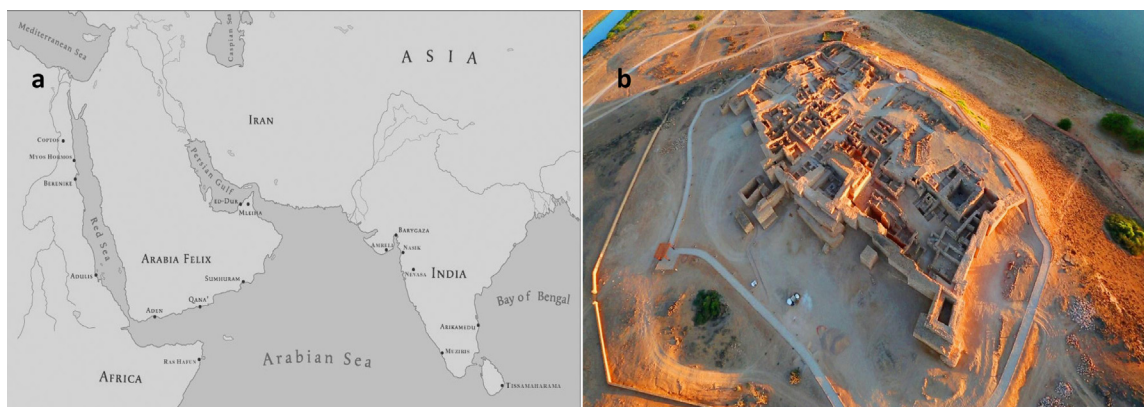
### 2.1. Reference substances

Synthesised 6,6'-dibromoindigo was kindly provided by Dr. Gundula Voss of the University of Bayreuth (Germany). Natural indigo, prepared from the leaves of *Indigofera tinctoria* following old recipes, was a gift from the Opificio delle Pietre Dure (Florence, Italy).

### 2.2. Samples

Twelve samples (Sum01, Sum02, Sum03, Sum04, Sum05, Sum06A, Sum06B, Sum07, Sum08A, Sum08B, Sum09 and Sum10) were collected from pottery vessels to determine the nature of the pink-violet materials. Samples Sum06A and Sum06B, which showed a different shade of colour, were collected from the same pottery shard; likewise Sum08A and Sum08B.

The shards belonged to different containers: open-mouth jars with ring bases in coarse and porous ware, large amphorae or generic containers, some showing traces of burning on the exterior. Sample Sum03, for example, was the base of a possibly Indian vessel. Sum01 was taken from a pottery shard probably belonging to a strainer, while Sum10 was collected from a complete jar with a wide mouth, standing on a ring base.



**Fig. 2.** a: the port of Sumhuram and the main centres involved in the Indian Ocean trade (3rd cent BC–5th century AD) (map A. Pavan); b: aerial view of the site of Sumhuram (the Italian Mission to Oman, IMTO archive).

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