PREHISTORIC TERRACOTTAS FROM THE LIBYAN TADRART ACACUS
Thermoanalytical study and characterization

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(Received May 3, 2002; in revised form November 2, 2003)

Abstract
The specimens studied in the present work consist of five terracotta fragments from an archaeological dig on the Libyan Tadrart Acacus massif, dating back to about 5000–8000 B.C.

The specimens were analysed using thermogravimetric analysis (TG, DTG), differential thermal analysis (DTA), thermomechanical analysis (TMA), X-ray diffractometry, IR spectrophotometry and inductively coupled plasma spectroscopy (ICP).

Analyses were aimed in particular to determine the most striking aspect of the finds, the difference in colour between the outer surface (reddish) and the darker inner portion of several of the specimens. The other main points investigated and discussed are related to the firing temperature and chemical and mineralogical composition, of terracotta specimens.

Keywords: infra-red spectroscopy, plasma emission (ICP), prehistoric terracottas, thermal analysis, X-ray diffractometry

Introduction
The study of ancient terracotta finds is of considerable archaeological interest as they represent one of the earliest artefacts produced by man. Their complete characterization can thus provide information concerning the technological, artistic and cultural level reached by the population of a geographical site in historical and even prehistoric times.

The results presented herein stem from physico-chemical analyses performed by different techniques on five terracotta specimens from an archaeological dig on the Libyan Tadrart Acacus massif. The material, presumably potsherds, with impressed decoration obtained using double-pointed comb-like instruments, probably dates back to between 5000 B.C. and 8000 B.C. [1].

The present research was aimed at: the complete physico-chemical characterization of the terracottas studied; investigation of the firing temperature of the fragments; identification of the cause of the different colouring taken on by the various outer or inner portions of most of these terracottas.

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The tests were performed using thermogravimetric analysis (TG), differential thermal analysis (DTA), thermomechanical analysis (TMA), X-ray diffraction (XRD), porosimetry, plasma emission spectroscopy (ICP), Fourier transform infrared spectroscopy (FTIR) and conventional microchemical techniques.

Among the analytical methods used in the present research, thermoanalysis and, in particular, three of the most important techniques related to it (TG, DTA and TMA) had a high analytical and guiding relevance. Moreover the importance of thermoanalysis' potential contribution to the characterization of many archaeological finds has been fully documented by researchers such as Wiedemann [2, 3], Odlyha et al. [4, 5] and Lamprecht [6]. More specifically, of the numerous works concerning the study of terracottas of different ages, carried out using mainly thermoanalytical methods suffice it to mention those of Mejdahl [7], Moropoulou et al. [8], Enriquez et al. [9] and Edwards et al. [10]. Furthermore, we deem to be of fundamental significance in this sector the thermodilatometric work done by Kiefer [11], Tite [12] and Roberts [13] on the determination of the firing temperature of ancient ceramics. This is an important problem as firing temperature depends above all on the characteristics of the kiln used, which to some extent reflect the technological level reached by the people making the products. For this reason, the study of terracotta firing temperature has been addressed by a number of workers, also using porosimetric (Morariu et al. [14]), thermal (Maggetti [15]) and more recently spectroscopic (Eiland and Williams [16] or Mirti [17]) methods. There is no doubt, however, that the thermodilatometric method as proposed and applied by the above-mentioned authors, together with the thermoanalytical observations, despite its drawbacks, perhaps represents the best known and most widely used method of those currently available. Also the present authors in recent years published some papers concerning the characterisation of ancient fictile statues and the values of their equivalent firing temperatures [18–20], or the analysis of wood finds [21–23] using thermal analysis.

**Experimental**

*Sampling, apparatus and methods*

The five terracotta finds examined, denoted for the purposes of this paper with the capital letters A→E (Fig. 1), were found during an excavation campaign carried out within the framework of a convention with La Sapienza University of Rome and ENEA [1], and come from an archaeological dig on the Libyan Tadrart Acacus massif known as the ‘Uan Telocat’ shelter, and all probably belong to pastoral period pottery and dating to between 5000 and 8000 B.C. [1]. The five specimens were first carefully ground up into a homogeneous powder to be used in the various analyses, except for porosimetric analysis, for which tiny fragments of the specimens not subjected to any pretreatment were used directly as they were sufficiently clean and bore no traces of soil.

The thermogravimetric and differential thermal analyses were performed using a Du Pont apparatus (951 Thermogravimetric analyzer and DTA cell) coupled to a Thermal Analyst 2000 Du Pont system. The experiments were carried out at a heating rate of