**Archaeology meets chemistry**

# Peeking into Pharaoh's * glass

* Ancient Egyptian sign for „Wine"

Details on viticulture in ancient Egypt are quite well understood by modern-day archaeologists. But what exactly was in Pharaoh's glass when he savored the gift of the wine gods – and was it just imbibed for relaxation and merriment or was it taken as a stimulating aphrodisiac or maybe prescribed by his physician to cure or alleviate pharaohnic ailments? Answers to these questions have eluded us for ages. When archaeologists recently consulted analytical chemists armed with thermal desorption GC/MS systems, information began to trickle out, offering insight into ingredients used in ancient Egyptian wine.

Wine from ancient Egypt is thought to have been honey-sweet – though now it is just bone-dry. What was once refreshing, stimulating and thirst-quenching has mostly evaporated; only dust and residues remain in the 3-5 millennia old amphorae that were found in the tombs of those ancient rulers and demigods, the Pharaohs. On their way to the netherworld, they were given gold and ample riches along with food and amphorae filled with precious wine. One amphora was marked: "Year 5. Wine of the House of Tutankhamen, Ruler of-the Southern On, the Western River. By the chief Vintner Khaa." (Source BBC).

Some tombs are embellished with wall paintings depicting scenes from ancient Egyptian vineyards (cf. picture on p. 22). From such graphical renderings, as well as from a separate hieroglyph for the word "wine", archaeologists were able to determine that grapes were being grown and wine produced as early as 3,000 B.C. in the Nile Delta (Lower Egypt). At that point a thriving wine-producing industry controlled by the rulers had already taken root. Vines were planted in pits filled with fertile Nile river silt. Given sufficient irrigation, vines could be grown successfully in oases.

## Sacrifices to the gods

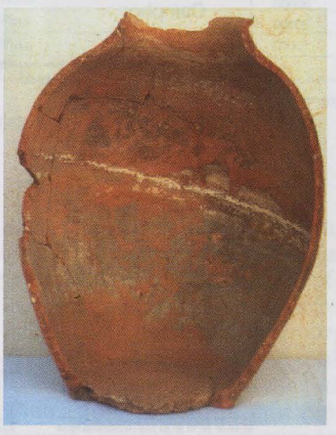
Archaeologists have found evidence that wine was well appreciated for festive occasions in ancient Egypt. The only drop of bitterness in the chalice was that many an outstanding droplet was reserved for the gods and donated as sacrifice. We have until now relied only on speculation as to what Tutankhamen and his contemporaries imbibed when "communicating" with the wine gods. The uncovered amphorae have been completely dry and empty; the wine evaporated an eternity ago. Not until chemists were called upon to inspect the grave goods more closely did hard facts begin to emerge. In the amphorae found in the grave of Tutankhamen, malvidine-3-glucoside was identified among the remains (*Armen Mirzoian et al., „Analytical Chemistry", Vol. 76, No. 6, March 15, 2004*).

**Polyphenols** are universally praised for their positive health effects, in large part ascribed to antioxidant and radical scavenging properties. One might also turn to grapes, raisins, black currants, cranberries or elderberries for a less stimulating source. Most chemical research on polyphenols is reportedly performed on wine.

This compound is one of the more stable anthocyanins, the group of compounds that lends a warm red hue to the class of wines known as red wines. The 18 year old Pharaoh, in other words, had been given amphorae of red wine to accompany him, possibly wine that he had favored during his short life. As an aside, anthocyanins form the main group of flavonoids that, along with phenols, make up the class polyphenols, which are thought to have positive health effects.

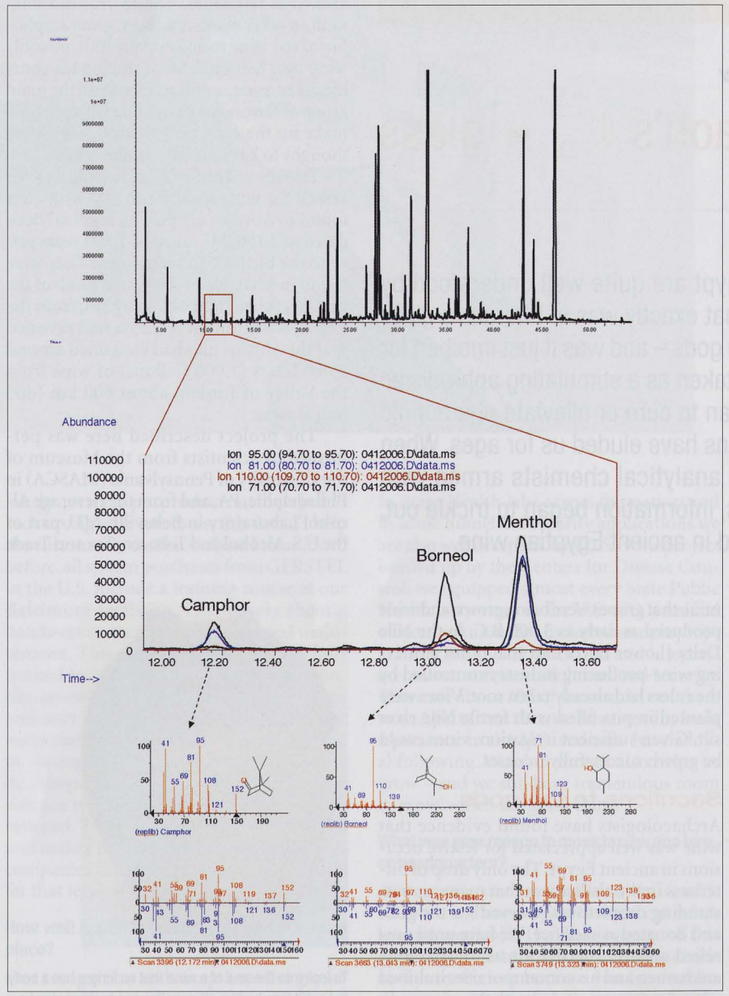
Equally scientifically intriguing was the search for wine residues in 700 wine jugs found in Abydos, Egypt. The jugs had been dated to 3,150 B.C., around 1,800 years prior to the birth of Tutankhamen. They were found in what was probably the tomb of the first Egyptian Pharaoh, Scorpion, from the first dynasty. Initial research had revealed that the Abydos jugs had contained around 4,000 Liters (1,000 Gallons) of wine from the Valley of Jordan, about 600 km (400 miles) away.

The project described here was performed by scientists from the Museum of the University of Pennsylvania (MASCA) in Philadelphia, PA, and from the Beverage Alcohol Laboratory in Beltsville, MD, part of the U.S. Alcohol and Tobacco, Tax and Trade



To look into the soul of a wine that no longer has a body, the scientists had no other option but to grind clay from the inside of the amphorae and jugs and extract wine-related substances from the granulate.

Mural in the tomb of Nebamun, soldier in the army of Pharaoh Thutmose IV (Photo: archive).




SPME Total Ion Chromatogram (top) of the Abydos sample and enlarged (12.00-13.60 min) Selected Ion Chromatograms (Middle), shown along with mass spectra and library mass spectra of select compounds (below).

Bureau (TTB). The scope of the project was to determine volatile and semi-volatile compounds in the wine residues, but not necessarily to determine the origins of the wine. In order to have a historically differentiated reference, a wine amphora from the Nubian town of Djebel Adda, dating back to the year 400 A.D., was analyzed as well.

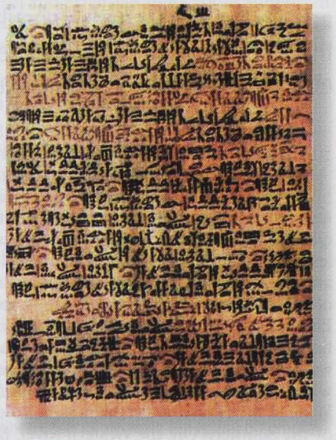
## Wine tasting based on pottery shards

To look into the soul of a wine that no longer has a body, the scientists had no choice but to grind the ancient pottery and extract the oenological residues from the resulting powder using acidic or alkaline solutions. The extracts were filtered and analyzed using chromatographic techniques. The following provides an overview of the methods used for analysis.

## Traces of resin and herbs

The results: In both samples, the scientists identified a range of terpenoids, esters and alcohols as well as various volatile compounds and L-tartaric acid. This was definitive proof that the amphorae and jugs had contained wine. Further, the identified compounds indicated that resin and herbs had been added to the wines, making them a kind of ancient day Retsina wine, possibly similar to what is produced, and mainly served to tourists, in Greece today.

The project provided facts that support the theory of a preference for wines enriched with resin and herbs at the court of the Pharaohs, covering the entire period from the beginning of the ancient Egyptian High Culture (Abydos find) until the latter parts (Djebel Adda find). The herbs may have been added mainly to produce a sought after taste or they could have been added for medicinal purposes. Herbs and tree resin were part of



Section of „Papyrus Ebers" (1,500 B.C.) a 20 meter long list of medicinal recipes, and thereby the most comprehensive documentation of medical knowledge in ancient Egypt known to man. The content mainly deals with internal diseases and their treatment. The papyrus was acquired for the University of Leipzig, Germany in 1872 by Georg Ebers (1837-1898), Professor of Egyptology.





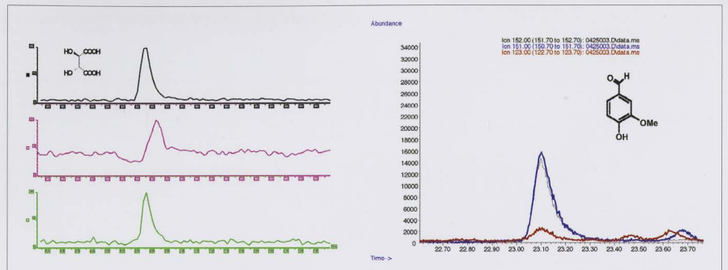
**Solid Phase Micro-Extraction (SPME)**
A 50/30 µm DVB/CAR/PDMS fiber was used. The fiber was immersed in a sodium chloride solution containing the sample powder inside the sample vial for 40 min. at a temperature of 80 °C. The concentrated analytes were desorbed from the SPME fiber in the GC inlet for 3 minutes at 250°C. The SPME process was automated using the GERSTEL Multi-Purpose Sampler (MPS).

**Gas Chromatography / Mass Spectrometry (GC/MS)**
A GC/MS system consisting of a 6890 GC and a 5973 MSD, both from Agilent Technologies, was used. Separation was achieved using a HP 5MS column, 30 m x 0.25 mm ID x 0.25 µm film thickness. Analyte transfer was performed in splitless mode, the MSD was set to scan mode from m/z = 40 to m/z = 400. GC oven program was started at 60 °C and programmed to 240°C at 3 °C/min. Carrier: Helium at 1.2 ml/min constant flow. Compounds were identified using mass spectral libraries and Kovats Retention Indices, calculated from a series of n-alkanes from $C_5$ to $C_{22}$.

**Thermal Desorption**
Residues from amphorae and jugs were also desorbed, or thermally extracted, using a Thermal Desorption System (TDS) from GERSTEL. The desorption temperature was programmed from a 50 °C starting temperature to 250 °C at a rate of 50 °C/min.

**Liquid Chromatography – Tandem Mass Spectrometry (LC/MS/MS)**
A Waters Acquity UPLC and a Micro-Mass Quattro Premier XE Triple Quadrupole mass spectrometer were used. LC parameters: UPLC BEH C18 column. Isocratic flow at 0.20 mL/min, 98 % $H_2O$ : 2 % ACN, 0.1 % Formic acid. MS/MS: Electron Spray Ionization (ESI), Cap. 4.50 KV, CV 20 V, CE 16 V.

the ancient Egyptian pharmacopoeia as we have learned from 13 ancient papyri with information on medicine and various recipes. Among these are the "Papyrus Smith" (2,500 B.C.), the "Papyrus Ebers" (1,500 B.C.) or the "Papyrus Hearst" (1,500 B.C.), all named after the people by whom they were later purchased. In "Papyrus Smith", diseases were clearly divided into incurable and curable afflictions; for the latter group, systematic instructions for treatment were listed. Knowledge about anatomy and physiology (e.g. functions of organs) was, however, very limited, which means that physicians at the time were quickly out of options for effective treatment. In many cases patients were diagnosed as being possessed by demons; prayers or redemptive magic was prescribed. Empirical work, religion and authorized magic often went hand in hand.




Multiple reaction monitoring (MRM) LC/MS/MS chromatogram traces of an L-tartaric acid standard (top) based on the m/z 149 and 87 molecular fragments. The middle and bottom traces are from the aqueous extracts of the samples from Abydos and Djebel Adda respectively.




Selected Ion Chromatogram of the peak at 23.13 min; retention time and mass spectrum match those of vanillin.

| RT (min) | Compound | Abydos | Djebel Adda | Possible origin |
|---|---|---|---|---|
| 3.75 | 1-Hexanol | x | | Wine |
| 5.81 | Benzaldehyde | x | x | Wine |
| 5.62 | Camphene | x | | Pine |
| 5.99 | Heptanol | x | | Wine |
| 6.27 | Phenol | x | | Mint |
| 6.48 | Menthene | x | | Mint |
| 7.68 | p-Cymol | x | x | Pine, Rosemary |
| 7.82 | Limonene | x | | Mint, Pine |
| 7.97 | Benzyl alcohol | x | | Wine |
| 9.27 | 1-Octanol | x | | Mint, Wine |
| 9.96 | Fenchone | | x | Rosemary, Fennel, Sage |
| 10.09 | 2-Nonanone | | x | |
| 10.91 | Phenethyl alcohol | | x | Wine |
| 10.92 | Fenchol | x | x | Pine |
| 12.17 | Camphene | x | x | Pine, Mint, Wild Fennel, Sage, Mugwort, Rosemary |
| 12.53 | γ-Heptalactone | | x | |
| 13.05 | Borneol | x | x | Pine, Rosemary, Mint, Oregano |
| 13.31 | 1-Nonanol | x | | Mint |
| 13.42 | L-Menthol | x | | Mint |
| 14.12 | α-Terpineol | x | | Pine, Mint, Wine |
| 14.46 | Ethyloctanoate | x | | Wine |
| 15.63 | Cuminaldehyde | | x | Rosemary |
| 16.41 | Carvone | x | | Mint, Yarrow, Wild Fennel, Sage, Mugwort |
| 17.57 | Ethyl Salicylate | | x | Wine |
| 17.67 | Decanol | x | | Mint |
| 18.55 | Thymol | x | | Mint, Wild Fennel, Sage, Basil, Thyme |
| 23.11 | Ethyl Decanoate | x | | Wine |
| 23.13 | Vanillin | | x | Rosemary, Thyme |
| 25.53 | Geranyl Acetone | x | | Rosemary |
| 35.34 | Farnesol | | x | Pine |
| 37.76 | Benzyl Benzoate | | x | Pine |
| 38.85 | Ethyl Palmitate | x | x | Wine |
| 45.76 | Ethyl Stearate | x | x | Wine |
| 46.28 | Manoyl Oxide | x | | Pine |
| 47.65 | Biformene | x | | Pine |
| 56.24 | Methyl Dehydroabietate | | x | Pine |

Compounds in the jugs from Abydos and amphorae from Djebel Adda identified using SPME-GC/MS and Thermal Desorption GC/MS.

A word on alcohol content of the wine in ancient Egypt: Alcohol plays a useful role as an extraction solvent for, and carrier of, active compounds in herbal medicine. The intoxicating role is of course equally well recognized and this seems to have been a cherished side-effect to what the doctor ordered. Beer, not wine, was the national beverage in ancient Egypt, often used in religious ceremonies and as a meal-time beverage. Legend has it that Osiris, the god of the underworld, taught humans how to brew beer. Prepared from malted barley, a type of wheat called emmer and date juice, beer was counted as a staple food on the same level as bread. Brewing beer was of course also a way of preserving drinking water and keeping it from being infested with undesirable microorganisms. Those ancient Egyptians who could afford it often preferred to drink wine when they wanted to have a good old time. Almost four thousand years ago, an Egyptian teacher lamented that one of his students was leading a debauched and alcoholized life. "Oh if only you would recognize that wine is a horror, if only you would forget the chalice".