



Method for direct mercury determination in vegetables using thermal decomposition - atomic absorption spectrometry



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INTRODUCTION

Mercury occurs in the environments as metallic form, inorganic salts and/or organometallic compounds. The earth's crust contains 0.5 mg kg^{-3} , ambient air may contain $0.002\text{-}0.02 \text{ pg dm}^{-3}$, and sea water contains about 0.03 mg dm^{-3} . Mercury is also found in trace amounts in most animal and plant tissues. Recent estimates of global emissions of mercury to the atmosphere are highly variable, ranging from 2 000 per year to 6 000 t year. Mercury compounds have been used as catalysts, fungicides, herbicides, disinfectants, pigments and for other purposes. The world production was about 10 000 t in 1973 and about 6 500 t in 1980. In addition to the production of pure mercury by industrial processes, mercury is released into the environment by human activities such as the combustion of fossil fuels, waste disposal and by industry. Recent estimates of anthropogenic emissions are in the order of 2 000 to 3 000 t per year [1].

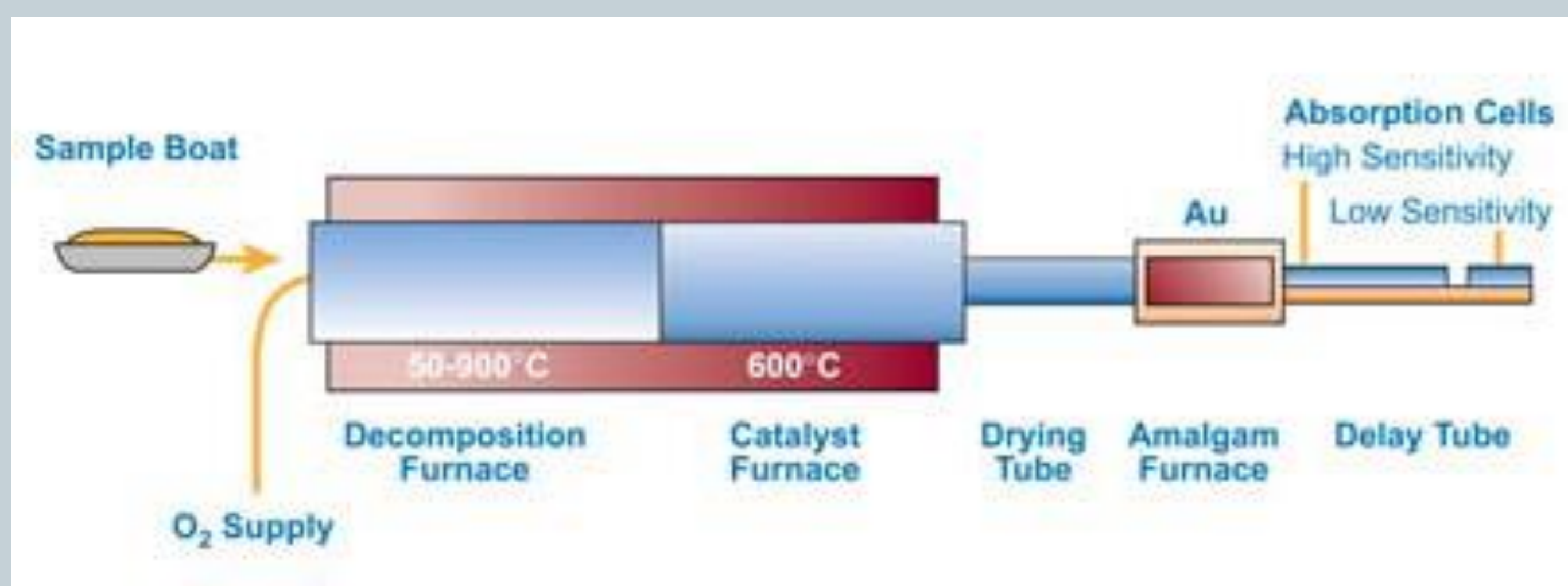
Hg poisoning may lead to damage in the central nervous system [2]. Hg is considered to be a global pollutant (UNEP 2002) because once in the atmosphere it can circulate for years before deposition. Relative high Hg concentrations were found in remote areas with no proximate sources of pollution, such as arctic region [3]. Hg can enter in soil through different ways: dry and wet atmospheric deposition or polluted wastewater. From soil this can enter through the food chain.

A variety of detection methods have been used for mercury determination. The most popular method for determining mercury in almost any type of sample has been based on cold vapour atomic absorption spectrometric measurement (CVAAS) and the technique is widely used. The way of liberating mercury from aqueous or digested samples is reduction, followed by volatilization and introduction of the mercury by aid of a gas stream. A gold amalgamation method to purify the mercury vapour can be used. After the organic vapour is purged out, mercury is released from the gold fibre trap by heating and then introduced into the spectrometer. The method can work not only for mercury purification but also for the collection and accumulation of mercury into a small volume which makes it possible to achieve elevated sensitivity.

For solid samples, Hg determination is difficult due to the high volatility of these element, and the digestion methods suppose sample heating. Direct Hg determination from solid sample is very important to obtain accurate results.

INSTRUMENTATION

The Hydra-C Direct Mercury Analyzer (Teledyne Leeman Lab, USA) provides Hg analyses from solid samples without sample pretreatment. The process involves combusting (decomposition) of a sample at high temperatures with oxygen. The evolved gases are carried through a heated catalyst to produce free mercury while removing halogens, nitrogen oxides, and sulfur oxides. The elemental mercury (Hg) are swept through a gold amalgamation tube. The amalgamation tube captures all of the mercury and is then heated to release the mercury, into a carrier gas which transports it into a cold vapor atomic absorption spectrometer (CVAAS). The transient signal is measured in series by a high sensitivity cell followed by a low sensitivity cell [4].



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EXPERIMENTAL

Soil and vegetable samples were collected from Ferneziu district of Baia Mare, NW of Romania, located near to plant ROMPLUMB, whose activity has caused extensive pollution of the area of lead and other metals for several decades.

From each sampling point, soil samples were collected at two different depths, at 0-10 cm and 10-20 cm, respectively. Also, from each sampling point vegetable grown on this soil were collected.

On the lab, the soil samples were air-dried, and sieved through 100 micron mesh sieve. The vegetable samples were dried in oven and grounded using a grinder. The samples were directly measured using the Hydra-C system. Table 1 shows the instrument parameters employed for soils and vegetables. For analysis nickel boats were used for all samples.

Table 1. Instrument parameters employed for solid samples

Parameter	Setting
Dry	300°C for 45 sec.
Decomposition	800°C for 150 sec.
Catalyst	600°C
Catalyst Wait Period	60 sec.
Gold Trap	700°C for 30 sec.
Measurement	90 sec.
Oxygen Flow	300 ml/min

Calibration was completed using aqueous standards prepared in 10% HNO₃. Working standards were blank, 0.1, and 1.0 ppm at several different injection weights. The calibration curve plots microabsorbance vs total mercury injected.

RESULTS AND DISCUSSIONS

In Table 2 the sampling points, Hg concentrations ($\mu\text{g/kg}$) in soil at 0-10 cm, 10-20 cm and in vegetable are presented.

Table 2. Sampling points, Hg concentrations ($\mu\text{g/kg}$) in soil and vegetable

Sampling point	Hg concentrations Soil 0-10 cm	Hg concentrations Soil 10-20 cm	Hg concentrations Vegetable
1	1253	1287	19.7
2	653	1480	53.4
3	983	1106	4.92
4	2004	2010	20.8
5	1050	930	4.6
6	815	797	11.5
7	1107	1033	3.05
8	855	806	49.6

In Romanian legislation the normal value for Hg concentration in soil is $100 \mu\text{g/kg}$. The alert threshold for sensitive areas is $1000 \mu\text{g/kg}$, and the intervention threshold $2000 \mu\text{g/kg}$. According to this, the measured concentrations in soil exceed the alert threshold in four surface samples and in five samples (depth 10-20 cm). In the samples 4 the intervention threshold is exceeded.

In the vegetables samples the Hg concentrations ranged between $3.05 - 53.4 \mu\text{g/kg}$. The calculated transfer factors for Hg from soil to vegetables ranged between $2.9 \text{ E-}3 - 62 \text{ E-}3$.

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