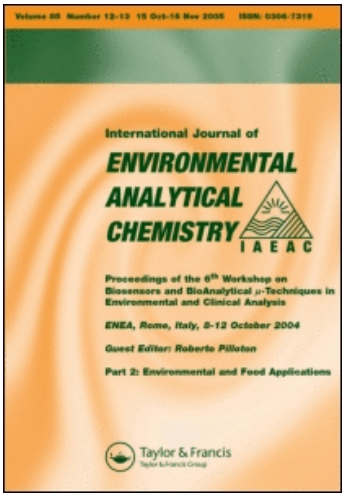

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Hydride Generation/Condensation System With an Inductively Coupled Argon Plasma Polychromator for Simultaneous Determination of Arsenic, Antimony, Selenium, Lead, Mercury and Tin in Honey

B. Jamoussi[a]; M. Zafaouf[a]; B. Ben Hassine[b]
[a] Département des Analyses Chimiques 23, Laboratoire Central d'Analyses et d'Essais, Montfleury, Tunisia [b] Faculté des Sciences de Monastir, Département de Chimie, Laboratoire de Synthése Organique et de Photochimie, Monastir, Tunisia

To cite this Article Jamoussi, B. , Zafaouf, M. and Hassine, B. Ben(1995) 'Hydride Generation/Condensation System With an Inductively Coupled Argon Plasma Polychromator for Simultaneous Determination of Arsenic, Antimony, Selenium, Lead, Mercury and Tin in Honey', International Journal of Environmental Analytical Chemistry, 61: 3, 249 — 256
To link to this Article: DOI: 10.1080/03067319508027239
URL: http://dx.doi.org/10.1080/03067319508027239

Intern. J. Environ. Anal. Chem., Vol. 61, pp. 249–256
Reprints available directly from the publisher
Photocopying permitted by license only

HYDRIDE GENERATION/CONDENSATION SYSTEM WITH AN INDUCTIVELY COUPLED ARGON PLASMA POLYCHROMATOR FOR SIMULTANEOUS DETERMINATION OF ARSENIC, ANTIMONY, SELENIUM, LEAD, MERCURY AND TIN IN HONEY

B. JAMOUSSI[1], M. ZAFAOUF[1] and B. BEN HASSINE[2]*

[1] *Laboratoire Central d'Analyses et d'Essais, Département des Analyses Chimiques 23, rue Jawaher Lel Nehru, Montfleury 1008, Tunisia,* [2] *Faculté des Sciences de Monastir, Département de Chimie, Laboratoire de Synthése Organique et de Photochimie, Monastir 5000, Tunisia*

(Received, 18 April 1994; in final form, 3 February 1995)

An efficient method for the determination of nanogram levels of heavy metals in honey is described. Honey samples obtained in the field from farms located along the coast of the province of Cap-Bon (North Tunisia) were analysed by hydride generation with an inductively coupled argon plasma polychromator after a previous treatment in a microwave acid bomb.

An apparatus for the generation of volatile hydrides, interfaced with an inductively coupled argon plasma polychromator for simultaneous determination of As, Pb, Sb, Hg and Sn, is used. The optimum conditions for generating and determining the compounds and the effect of different parameters are discussed. The parameters investigated include: the chemical nature, form and concentration of the reductant, acid concentration of the sample and the carrier gas flow rate. Detection limits range 0.05 ng/ml for Hg to 1.1 ng/ml for Sb and precision values at 10 ng/ml are less than 6% of the relative standard deviation. Analytical protocols concerning analytical stages are exposed and discussed.

KEY WORDS: Honey, hydride generation, ICP, heavy metals.

INTRODUCTION

Recent epidemialogical studies have indicated the occurence of certain cancers and cardivasculars diseases with the presence of trace metals such as Hg, Pb, As and Se in food[1].

Many investigations[2-16] have demonstrated that hydride generation(HG), followed by the introduction of gaseous hydrides into an ICP-AES, is a suitable method for the determination of several trace elements, for which detection limits with conventional pneumatic nebulization are not sufficient to direct and control real-life concentrations in biological environmental and food samples. In addition, HG-ICP-AES provides the

* Corresponding author.

opportunity to simultaneous the determine the hydride-forming elements of interest namely: arsenic, antimony, mercury, lead, tin and selenium.

Honey as natural sweetener enjoys an increasing popularity among consumers. As some sources say that "no other food can contains as many different known toxicants as honey"[17], it is important to check its quality. Although various workers have reported heavy metal residues in honey bees[18,21,22], honey[17,19-24] and wax[22], it is found that there are only few analytical methods dealing with these kind of samples.

A variety of sample dissolution procedures have been shown to be suitable for the determination of arsenic[3,6,7,19], selenium[10,15,20], arsenic and selenium[9], mercury[10,21], lead[14,23], tin[12,24] or simultaneously of aresenic, antimony and selenium[25], in various materials.

However, to our knowledge no digestion procedure specific for honey has been described in the literature permitting the simultaneous determination of all six elements with HG-ICP-AES. For this reason it could be highly desirable to develop a rapid and accurate method for their analysis.

Considered as an analytical sample, honey represents a complex matrix requiring previous mineralization before most of the analytical techniques proposed so far can be used. The most widely accepted approach currently seems to be the use of microwave to accelerate the digestion of the sample, which is placed in a closed recipient and subjected to acid and high pressure. The merits of pressurized acid digestion in closed or semi closed vessels, particularly the low risks of contamination and volatilization losses, are widely recognized, and it is not surprising that such techniques are attracting considerable attention.

This report describes the application of a simple continuous hydride generation system coupled with a low power (1.2 Kw), ICP for the determination of arsenic, antimony, selenium, tin, mercury and lead in honey samples. A procedure utilizing microwave dissolution in a closed teflon bomb and hydride generation reaction conditions were evaluated in an attempt to establish optimal conditions for simultaneous determination of all six elements. The method was applied to the determination of heavy metals in honey samples from northern Tunis, in order to have an idea of their contamination degree and know whether they are suitable for consumption.

EXPERIMENTAL

Reagents

Distelled deionized water with a metered resistance of 18 mΩ and ultrahigh purity commercial acids were used for all solution preparations. Standard solution of inorganic arsenic, antimony, tin, mercury, lead and selenium were prepared by dilution from commercially available 1000 mg/l stock solution (Wako pure chemical industries). For the arsenic and antimony determinations, a 8% (w/v) NaI prereductant solution was used. The peroxodisulfate solution (oxidizing agent for lead and tin determination) was made by dissolving 6 g $(NH_4)_2S_2O_8$ in 100 ml of water.

Apparatus

A Schimadzu ICPQ/V-1014s vacuum optical emission spectrometer was used for inductively coupled plasma studies. The spectrometer was designed for measuring and

analysing the spectral lines of a wavelength range of 190 nm or more. Instrumental parameters are given in Table 1.

The samples were mineralized in an acid digestion bomb by a MDS-81D(CEM) microwave oven.

Hydride generation (Schimadzu HYG-1) was accomplished in a continuous mode using a two chanel peristaltic pump(Perista pump chromatograph alta) to eliver sample and reagent to an injector fitting.

Sample preparation

Mineralization was carried out in two stages: 10 g of honey were dissolved in 10 ml of water in a digestion vessel placed in an ice water bath, and 10 ml of concentrated H_2SO_4 were added. Concentrated HNO_3(15 ml) was then added to the mixture by small increments (1 ml). After cooling, the digestion vessel was placed in the microwave oven. The first working cycle of the microwave oven is given in Table 2a.

The digests were cooled, 10 ml of HNO_3 were added by small increments to the sample-acid mixture in an ice water bath, and the mineralization was completed by the second working cycle of the microwave digestion system (Table 2b).

Mineralization was completed in 20 min, after the digestion bomb was cooled by freezing at −18°C for 35 min. A few drops of H_2O_2 were added for complete oxidation, and the resulting solutions were transferred to 100 ml volumetric flasks. Concentrated HCl(15 ml) was added to each flask and the solution diluted to 100 ml with distilled deionized water.

RESULTS AND DISCUSSION

Optimum operating conditions

By use of the previous literature on hydride generation ICP-AES as a guide, a brief investigation of the effects of various operating parameters on sensitivity and detection limits was conducted. The optimum ICP instrumental values obtained are summarized in Table 1.

Hydrochloric acid is practically the best acid used for generating arsenic, mercury, antimony hydrides although occasionally an HCl-HNO_3 mixture has been proposed. Our experiments showed that the optimal HCl concentration range was 1–2 M. The readings obtained with higher and lower acid concentrations can be interpreted as being due to slower generation (when [HCl] <1 M) and to poorer transport due to excessive hydrogen generation (when [HCl] >1 M). The concentration and flow rate of the reducing agent are also of great importance for the yield generated, and are also related to the acidity of the medium, since the generation reaction involves the formation of hydrogen gas, which consumes protons from the medium together with the reducing agent.

Therefore, the influence of the sodium borohydride concentration was studied at the three optimum acidities: 1; 1.5 and 2 M HCl. Table 3 shows the effect of the $NaBH_4$ concentration on the AsH_3 signal of an acid solution of As (III) 50 ng/ml at different HCl concentrations. In all three cases, at low concentrations of $NaBH_4$, generation is slow and the intensity of AsH_3 decreases. When the concentration of the reducing agent is higher (20 or 30 g/l), the yield is higher, but the reaction produces more hydrogen (plasma

Table 1 ICP-AES operating parametres.

	ICP Polychromator
Forward power	1.2 KW
Argon cooling gas	14 l/mn
Focal length	1000 mm
Polychromator	Paschen run mounting
Linear dispersion	0.467 nm/mm
Outer slit	30 μm
Wavelengths (nm)	As: 279.55; Sb: 217.59; Hg: 253.65; Pb: 220.35; Se: 196.09; Sn: 189.99
Integration time	10 s
	Hydride generation reaction
Flux argon $NaBh_4$	0.4 l/min
Flux argon sample	0.6 l/min
HCl concentration	1.5 M
$NaBH_4$ concentration	6 g/l in NaOH 0.1 M

becomes unstable), and this effect increases as the HCl concentration increases. The best results were obtained in all cases with 0.6% $NaBH_4$ using 1.5 M HCl.

Finally the influence of the carrier gas affects the precision of the method. When the flow rate is low, the gas reaches the ICP slowly and the intensity of MH_n(M = As, Pb, Sb, Se; n = 3 or 4) and Hg° increases. On the other hand, high flow rates greatly dilute the hydride, so that the intensity of MH_n or Hg° is reduced. Figure 1, gives the emission intensity of the heavy metals studied as function of the carrier gas flow rate.

Prereduction studies

The oxidative attack used in many of the digestion procedures leaves arsenic and antimony in (+V) oxidative state and selenimu in the (+VI) oxidative state. Several

Table 2(a) First working cycle of the microwave oven.

Stage program	*Base time (min)*	*Actual power (watt)*
1	2	150
2	9	0
3	8	100
4	4	0

Table 2(b) Second working cycle of the microwave oven.

Stage program	*Base time (min)*	*Actual power (watt)*
1	15	150
2	5	0

Table 3 The effect of $NaBH_4$ concentration on intensity of AsH_3 at different HCl concentration.

[$NaBH_4$]	*1.0 M HCl*	*1.5 M HCl*	*2.0 M HCl*
0.2%	0.0714	0.0749	0.0732
0.6%	0.0876	0.0983	0.0782
0.8%	0.0743	0.0799	0.0761
1.0%	0.0746	0.0835	0.0861
2.0%	unstable	unstable	unstable

previous works[3,6,7] have reported the reduction of As(+V) and Sb(+V) to the (+III) oxidation state, prior the hydride generation, by the addition of potassium iodide, for maximum hydride generation. Unfortunately, this procedure also reduces selenium and mercury to the zero oxidation state, from which no hydride is formed. Although the determination of As, Sb, Sn, Pb and Se were commonly performed sequentially in our laboratory by using a separate procedure described below (a/, b/, and c/). The method was developed with simultaneous determination of all six elements in mind. Thus, the development of a single procedure for the simultaneous determination by HG-ICP-AES requires careful consideration not only of the oxidation-reduction chemistry of these elements and its influence on the hydride generation process but also of the chemistry of dissolution of these elements(mineralization).

In the present work, this can be achieved only if arsenic and antimony are determined as As (+V) and Sb (+V) and the reduction of Hg (+II) to Hg° and Se (+VI) to Se° by potassium iodide could be avoided.

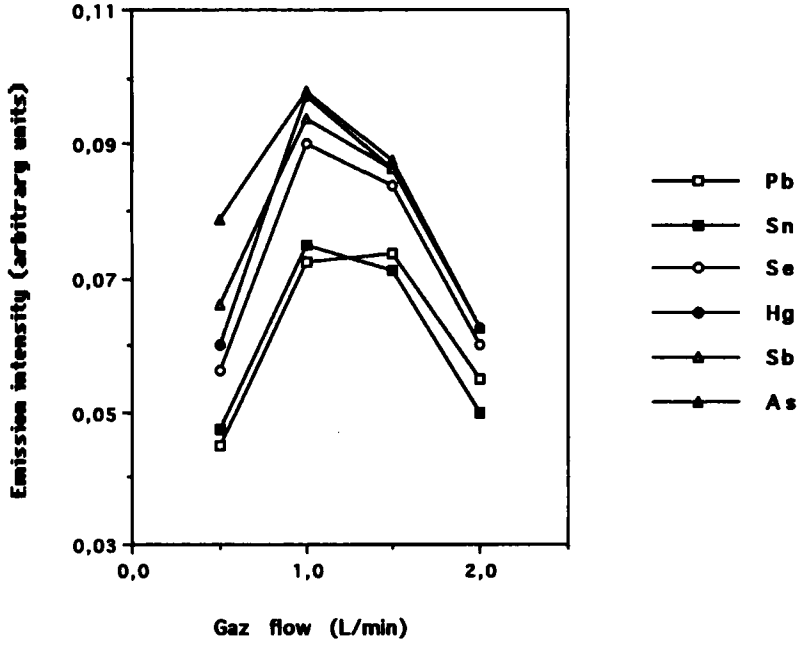

Figure 1 Influence of increasing carrier gaz flow rate(in L/mn) on the ICP-AES signal of (Pb, As, Se, Sn, Hg and Sb at 50 ng/ml) with hydride generation.

a/ Determination of lead and tin

The efficiency of the reduction of Pb (+II) to plumbane (PbH_4) and Sn (+II) to stannane (SnH_4), was not very good (commonly 16–60%). Improvement of the procedure sensitivity and more complete hydride formation can be obtained by addition of an oxidising (peroxodisulfate in the present case) which transform the lead and tin into the metastable Pb (+IV) and Sn (+IV) form before reduction.

The best conditions for the determination of lead or tin were obtained with a known amount of the acidified sample digest (about 5 g was mixed with 6 ml of concentrated hydrochloric acid). An oxidiser (1 ml of peroxodisulfate 6%) was added. The solution was diluted with water to 50 ml in a volumetric flask. Standard and reagent blanks were treated similarly.

b/ Determination of arsenic or antimony

An aliquot of the acidified sample digest was transferred to a flask and diluted to 20 ml with the acid diluent. The NaI prereductant (10% W/V) was added to the flask: 0.5 ml is sufficient to reduce As (+V) or Sb (+V) to the trivalent state. A minimum of 1 min reaction time is required to prereduce the As and Sb. Standard and reagent blanks were treated with the NaI prereductant prior to hydride generation.

The prereductant is essential to the generation of stibine, SbH_3, under the uniform conditions of acidity (10% H_2SO_4: 15% HCl) used throughout for As and Sb. Arsine, AsH_3, is quantitatively produced either in the presence or absence of the NaI.

c/ Determination of selenium and mercury

Sample, blank and standard aliquot for Se and Hg determination are treated just like those for As or Sb determination with the important exception that no prereductant is added. A prereductant would prevent generation of H_2Se and Hg by possible reduction to the element form.

d/ Detection limits

Detection limits were determined for all six analytes in a 10% H_2SO_4: 15% HCl (V/V) mixture, and correspond to the concentration of anlytes equivalent to twice the standard deviation of the signal obtained from the consecutive determination of six blank digestions taken through the entire procedure. The obtained results (Table 4) show a detection limit within the values 0.05–1.1 ng/ml.

e/ Precision

Precision studies were made with two concentrations of standard solution, 10 ng/ml and an amount approximately five times the detection limit, were each determined five times in a four hours period. Table 5 illustrates the precision of the technique for standard solution.

Table 4 Detection limit (ng/ml).

Element	*Detection limit*
Hg	0.05
Sn	0.52
As	0.60
Se	0.80
Pb	1.00
Sb	1.10

Table 5 Precision.

Elements	*Standard(ng/ml)*	*RSD(%)*	*Standard(ng/ml)*	*RSD(%)*
Hg	10	2.1	0.5	2.3
Sn	10	2.3	3.0	2.5
As	10	2.5	3.0	2.8
Se	10	3.4	4.0	4.0
Pb	10	5.4	5.0	7.5
Sb	10	5.2	5.0	6.0

f/ Recovery

Recovery studies were made by spiking the honey sample just prior to the digestion procedure with varying amounts of standard solutions.

Quantification of As, Sn, Se, Sb, Hg and Pb was made from the linear calibration curve verified by the method of standard additions. The results of the standard recovery for the six elements of interest carried through the digestion procedure are shown in Table 6. Values for the recovery of predigestion spikes were generally quantitative. However, the low recovery for Sb and Pb were probably due to incomplete oxidation of Pb (+II) and Sb (+III) using H_2O_2 as an oxidiser reagent.

Application

The technique was found to be both precise and reproducible and the mineralisation in a microwave acid digestion bomb is less complicated and time-consuming than

Table 6 Digestion recovery.

Element	*Sample quantification (ng/g)*	*Amount (ng/g)*		*% recovery*
		added	*recovery*	
Hg	38.0 ± 0.5	10	45–51–49	104 ± 2
Sn	96.0 ± 5.2	10	102–101–104	96 ± 2
As	54.0 ± 6.0	10	65–63–65	99 ± 3
Se	82.0 ± 8.0	10	88–86–90	94 ± 2
Pb	73.5 ± 10.0	10	72–74–75	88 ± 2
Sb	20.0 ≠ 11.0	10	25–22–18	72 ± 111

Table 7 Mean concentrations (in ng/g) of heavy metals in honey sample from the coast of the province of Cap-Bon (Tunisia).

Sample	*Hg*	*Sn*	*As*	*Se*	*Pb*	*Sb*
Nabeul(3)	38	96	54	82	73	20
Hammamet(1)	25	72	32	43	51	18
Beni-Khiar(7)	27	63	35	52	68	24
Kelibia(2)	22	69	42	61	59	29
Slimane	24	57	51	41	57	21

conventional dissolution techniques. The small volume of acid used and the minimal handling of a few reagent decrease the chance of contamination, an important factor in trace element analysis.

This method has been found appropriate for routine laboratory analyses. In order to check the quality of honey, seventeen samples were obtained directly from farms located along the coast of the province of Cap-Bon(Tunisia) Table 7 lists the average concentrations of metals in the honey sample study that are lower than the safety levels established by the WHO.

References

1. J. M. Concon, in: *Food Toxicology, Part B* (Dekker, New York, 1988) pp. 1043.
2. M. Thompson, B. Pahlavanpour and S. J. Walton, *Analyst.*, **103,** 568–579 (1978).
3. R. C. Fry, M. B. Denton, D. L. Windsor and S. J. Northway, *Appl. Spectrosc.*, **33,** 339–403 (1979).
4. B. Pahlanvanpour, M. Thompson and L. Thorme, *Analyst.*, **105,** 756–761 (1980).
5. B. Pahlanvanpour, J. H. Pollen and M. Thompson, Analyst., 105, 274–278 (1980).
6. J. A. C. Broekaert and F. Lels, *Fresenius Z. Anal. Chem.*, **300,** 22–27 (1980).
7. T. Nakahara, *Anal. Chim. Acta.*, **131,** 73–82 (1981).
8. K. A. Wolnik, F. L. Fricke, M. H. Hahn and J. A. Caruso, *Anal. Chem.*, **53,** 1030–1035 (1981).
9. P. D. Goulden, D. H. J. Anthony and K. D. Austen, *Anal. Chem.*, **53,** 2027-2-29 (1981).
10. D. D. Nygaard and J. H. Lowry, *Anal. Chem.*, **54,** 803–807 (1982).
11. M. Navaraco, A. M. C. Lopez, M. M. Sanchez, V. H. Lopez and G. de la Serrana, *J. Agric. Food. Chem.*, **39,** 2223–2225 (1990).
12. N. Hisatake and I. Masahiko, *Fresenius. J. Anal. Chem.*, **336,** 5–7 (1990).
13. M. C. Valdés-Heria Y. Tamprano, M. R. Ferrnandez de la Campa and A. Sanz-Medel, *J. Anal. At. Spectrom.*, **8,** 847–852 (1993).
14. M. C. Valdés-Heria Y. Tamprano, M. R. Ferrnandez de la Campa and A. Sanz-Medel, *J. Anal. At. Spectrom.*, **8,** 821–825 (1993).
15. H. Tao, J. W. Lam and J. W. McLaren, *J. Anal. At. Spectrom.*, **8,** 1067–1073 (1993).
16. B. Welz and M. Sucmanova, *Analyst.*, **118,** 1417–1423 (1993).
17. N. Sutlupinar, A. Mat and Y. Satganoglu, *Arch. Toxicol.*, **67**(2), 148–150 (1993).
18. J. Rostkowski, N. Omieljaniuk and M. Borawska, *Bromato. Chem. Toksykol.*, **25,** 391–397 (1992).
19. H. Sevimli, N. Bayulgen and A. Varinliogen, *Kim. Muhendisligin*, **4,** 237–241 (1992).
20. P. Z. Trstenjak, M. G. J. Mandic and B. J. Zdravko, *Lebensm-Rundsch.*, **89**(2), 46–48 (1993).
21. J. Toporcak and J. Legath, *Vet. Med.*, **37**(7), 405–412 (1992).
22. F. Schmutzler, *Wiss. Umwelt.*, (3–4), 117–120 (1991).
23. H. Raes, R. Cornelis and U. Rzeznik, *Sci. Total Environ.*, **113,** 269–279 (1992).
24. C. Shi, W. Tsai and W. Chong, *At. Spectrosc.*, **13,** 185–189 (1992).
25. M. H. Hahn, K. A. Wolnik, F. L. Fricke and J. A. Caruso, *Anal. Chem.*, **54,** 1048–1052 (1982).