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Trace Analysis of Mineral Elements in Raw Materials and Finished Products in the Chocolate Industry

I. Study of the Mineralization of High Fat Content Samples with HPA* Apparatus for the Determination of Lead and Cadmium Ultratrace Content by Electrothermal Atomic Absorption Spectrometry

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Introduction

For the trace analysis of mineral elements held in products with a high percentage of fat such as cocoa beans, cocoa nibs, cocoa liquor, hazelnuts, whole milk powder, various types of chocolates, . . . , the most difficult problem resides in the preparation of the samples. It is not only a question of putting quantitatively into solution the traces of metal to be analyzed, but also to destroy totally the fat present and all other organic matter in these samples. An insufficient mineralization which still leaves part of the fats undigested in the solution leads to unwanted interference during the measurement. For example, for the determination by electrothermal atomic absorption spectrometry (ET-AAS) of lead and cadmium, it can be observed that the presence of undestroyed fats in the analyzed solutions gives a non-specific background signal so strong that it cannot be correctly compensated. This fact decreases the accuracy of the measurement even when the quantities of fats are not very high and makes the analysis impossible when faced with high fat contents.

Nevertheless, it is specially because of the toxicity of heavy metals that both authorities and manufacturers are uniting their efforts for setting up valuable methods of determination. During the last years, food legislation has become active with regard to these contaminants. Proposed guidelines and maximum admitted levels are being given (1–6). At the same time, the questions raised by certain consumers should be taken into consideration. Thus all concerned people must correctly receive information on the content of these elements in foodstuff, and that based on accurate results. For these reasons, our laboratory should develop a reliable method.

* High Pressure Asher

This paper describes the advantages of using the HPA to mineralize high fat content samples in view of determining up to 0.05 ppm Pb and 0.01 ppm Cd with good accuracy.

Methods of mineralization

The general methods proposed in the literature for the mineralization of food samples can be divided into two main categories: dry ashing and wet digestion. A comprehensive literature survey of these sample preparation methods was published in 1980 by *Blake* (7).

The dry ashing, usually done by calcination in platinum crucibles, may be used in quite good conditions to determine non-volatile elements found in rather high concentrations. For example, elements such as Fe, Cu, Zn may be satisfactorily analyzed in cocoa products by AAS after such a mineralization.

However, for elements like Pb, Cd, Hg, As and others, especially if they are at the trace or ultratrace level, a dry ashing cannot be considered because of the losses through volatilization.

For the analysis of the volatile elements, the wet digestion must be used. For this, some procedures, different mixtures of acids, as well as specially designed apparatus have been proposed.

First, in our laboratory one of the mineralization devices using a refluxing heating system was tried. With the help of this system, the digestion of the samples is carried out with nitric acid in some quartz flasks which are heated in a bath of inorganic melted salts. The apparatus can lead to satisfactory results for certain products, but for samples with high fat contents such as cocoa beans and by-products, it was judged unsuitable to determine Pb and Cd at ultratrace level. For instance, our trials showed that even with long mineralizations – through the night and up to two days – a total destruction of the fat in a cocoa liquor cannot be managed. This leads to a bad correlation between the specific and the non-specific signals in the determination of lead and cadmium content by ET-AAS. In figures 1a and 2a, we have shown the graphs of the atomic absorption obtained for the determination of lead and cadmium in a cocoa liquor mineralized by this method. The high background signal is due to the incomplete mineralization. It is also to be noted that the long time of the mineralization and the fact that a large volume of acid has to be added increases the danger of contamination of the analyzed sample.

Using the same principle *May* and *Stoeppler* (8) have shown that the mineralization can be improved in a quartz vessel with a cap held by springs allowing a light overpressure. The beneficial effect of the cumulative action of the pressure and the temperature for the wet digestions with nitric acid is still more evident using the mineralization bombs. Such bombs used as closed digestion systems are proposed by various firms like Perkin-Elmer, Berghof, Paar, Prawol, Uni-Seal, etc. Added installations allow a controlled heating with a programmer.

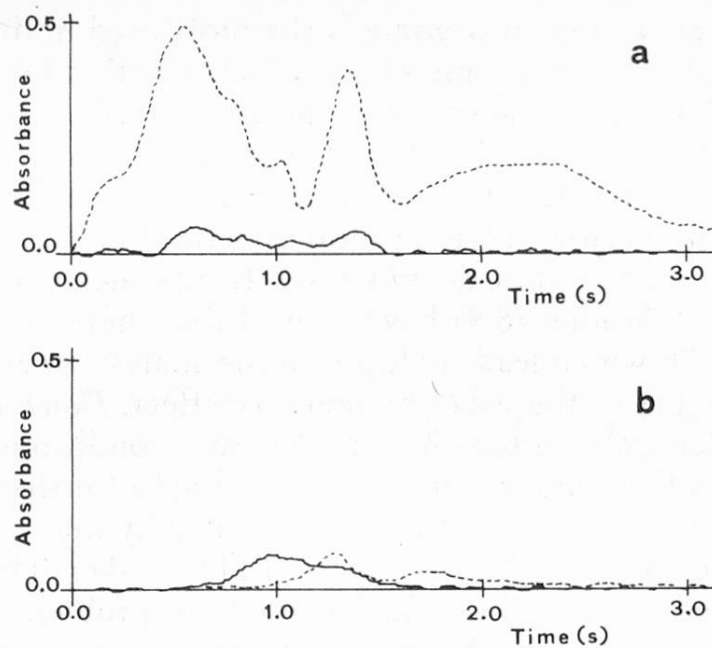


Fig. 1. Diagrams absorbance / time obtained for the Pb determination in a chocolate mass: background-corrected analytical signal — solid line; background tracing — dotted line. Conditions of determination by ET-AAS with graphite oven according to table 1:

- a mineralized 8 hours with HNO_3 in the device working at the ambient pressure
- b mineralized with the HPA according to operating procedure

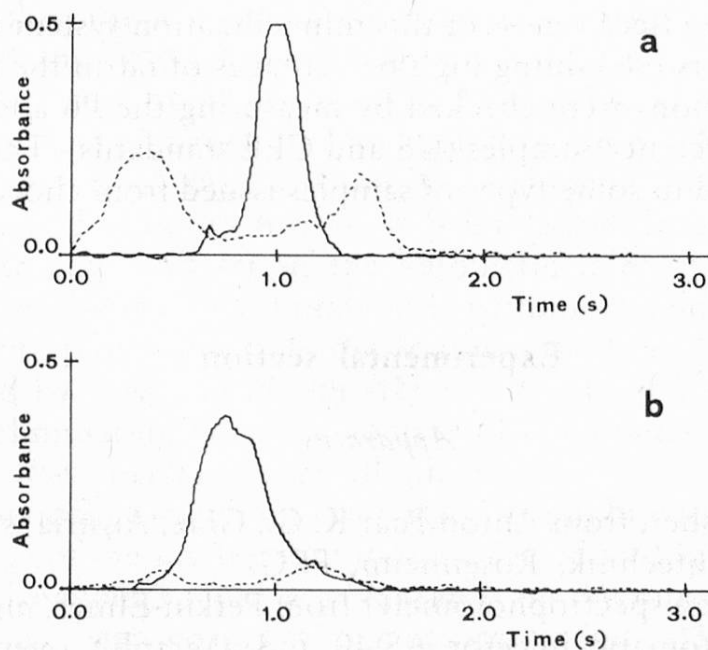


Fig. 2. Diagrams absorbance / time obtained for the Cd determination in a chocolate mass: background-corrected analytical signal — solid line; background tracing — dotted line. Conditions of determination by ET-AAS with graphite oven according to table 1:

- a mineralized 8 hours with HNO_3 in the device working at the ambient pressure
- b mineralized with the HPA according to operating procedure

This type of mineralization procedure is the most used in different laboratories dealing with analyses of trace metals in products with a high content of fat.

The trials carried out in our laboratories showed indeed a significant improvement of the correlation analytical signal / background signal in determinations by atomic absorption after mineralization in bombs under pressure. But some problems still remain because polytetrafluorethylene (PTFE) beakers are used as containers since the quartz ones do not resist to the mechanical loads during such a mineralization. Studies (8,9) have proved that there is an adsorption on the surface of the PTFE which leads to losses in the analysis or even to a contamination from one sample to the other by memory effect. *Döscher* and *Knöbel* (10) mentioned that under high temperature and pressure conditions the gas permeability of PTFE causes the condensation of the acid used for the digestion on the inner metallic wall of the bomb. So the wall is eroded by the acid and the resulting products may be fixed on the wall of the PTFE beaker. This makes the decontamination procedure more difficult. To avoid this problem, the authors proposed the use of titanium bombs. Moreover, the rather long mineralization time as well as the fact that a set of bombs must be used to carry out several mineralizations simultaneously represent drawbacks for this procedure.

As a perfected system of wet digestion under pressure, the apparatus «High Pressure Asher» (HPA) has enabled us to circumvent the inconveniences of the pressure bombs and to mineralize satisfactorily within acceptable time of 2–3 hours in some quartz containers, up to seven samples per load. This apparatus was presented by the author who developed it (11) and in the present article, we propose to show the effectiveness of this mineralization system for raw materials and finished products containing high percentages of fat in the chocolate industry. The mineralizations were checked by measuring the Pb and Cd values with ET-AAS in some reference samples (US and CEE standards). Then these two elements were analyzed in some types of samples issued from chocolate manufacture.

Experimental section

Apparatus

- High Pressure Asher, from Anton Paar K. G., Graz, Austria, supplied by Hans Kürner, Analysentechnik, Rosenheim, FRG.
- Atomic absorption spectrophotometer from Perkin-Elmer, model 3030 equipped with an automatic injector AS-40 and a graphit oven HGA-400.
- Quartz vessel consisting of: cups for the automatic injector AS-40, 50 ml volumetric flasks and 5 ml test tubes.
- Steaming apparatus for cleaning the quartz vessel with nitric acid steam from Hans Kürner, Analysentechnik, Rosenheim, FRG, with an extra 22 branches steam distributor for the test tubes and cups cleaning.
- Purifying system of water, from Millipore, model Milli-Q.

- Laminar flow clean air hood, from Skan AG, Basle, special execution with high-efficiency particulate air filter and active coal filter.

Reagents and solutions

- Nitric acid 70% «Baker-Instra-Analyzed».
- Concentrated standards of Pb and Cd at 1000 ppm, from J. T. Baker Chemicals.
- Six combined diluted standards of Pb and Cd prepared in cleaned 50 ml volumetric quartz flasks containing from 10 ppb Pb and 1 ppb Cd to 60 ppb Pb and 6 ppb Cd.

Procedure

Representative samples of about 0.35 g are precisely weighed in the quartz tubes of the HPA's sample holder. 2 ml concentrated HNO₃ are added and the tubes are placed, along with a blank, in the HPA. The mineralization procedure takes about two hours at 270 °C under 115 bar nitrogen. Then, after 45 min cooling, the quartz tubes are taken out and the nitric solution shows a bluish colour, except for the blank which is yellowish. Under the protection of the laminar flow hood, using the 2 ml gauge on the tubes, these are refilled first up to this level with pure water, then the walls of the tubes are rinsed with 3 more ml of water to reach a final volume of 5 ml. This is after homogenized.

For the measurement by ET-AAS, the spiking method is used. For each sample, seven solutions are prepared. In 5 ml quartz test tubes 0.5 ml of pure water or respectively of each from the six combined standard solutions are added to 0.5 ml of mineralized solution. After homogenisation the solutions are transferred in the quartz cups and set in the automatic injector.

All quartz vessels were cleaned previously with nitric acid in the steaming apparatus, rinsed with pure water from the Millipore system and if necessary dried.

As mentioned by *Wolf and Harnly* (12) an attitude of a «useful paranoia» in evaluating and eliminating potential sources of contamination in every step of the entire study was maintained at all times.

The electrothermal atomization takes place in graphite tubes with L'vov platforms inside. 20 µl of the sample solutions are introduced by the injector on the L'vov platform. To avoid a rapid degradation from the nitric acid solutions, the graphite tubes have been coated with tantalum carbide (13). The heating programming of the graphite oven is done in table 1.

The areas of the atomic absorption peaks at 283.3 nm for Pb and 228.8 nm for Cd were measured. These values are corrected for the background absorption and for the value of the blank.

For each solution, the AAS apparatus has been programmed to calculate the average of three injections. The regression curve for the seven solutions corre-

sponding to one mineralized sample allowed us to determine the metal content. In order to stay in the linear absorption field which is mandatory to determine the right regression curve using the spiking procedure, the concentration levels of the mineralized samples diluted to 5 ml must not be higher than 70 ppb of Pb and 7 ppb of Cd, according to our experimental conditions. This corresponds approximately to a level of 1000 ppb Pb and 100 ppb Cd in the solid samples. Higher concentrations must be appropriately diluted after mineralization.

Table 1. Graphite oven programs for Pb and Cd atomisation

Step	Temp. (°C)		Ramp time (sec)	Hold time (sec)	Argon flow	
	Pb	Cd			Pb	Cd
1. Drying	90		10	10	purge	
2. Drying	120		10	10	purge	
3. Thermal pretreatment	500	400	10	20	purge	
4. Atomisation	2100	2000	0	5	stop mini*	
5. Conditioning	2650		1	3	purge	
6. Cooling	40		10	1	purge	

* Mini flow of 80 ml/min.

Results and discussion

The HPA apparatus presents much broader possibilities with regard to the temperature programme. It allows to programme and run up to five-sectional temperature profiles. The possibility of installing a pressure sensor which measures the pressure inside the quartz tube during mineralization is another potential advantage. The later allows to optimize the mineralization conditions for each type of sample. This depends on its nature, specially on the percentage and the type of the fat held.

Because the device for inside pressure measurement is not available yet, we could not beneficiate from it to optimize the mineralizations of the samples of different natures. Thus it is certain that for part of the samples we analyzed, we should have had a lower digestion temperature and specially a shorter digestion time. This is the reason why the conditions given can only be taken as first indications. They represent strong conditions which have enabled us to mineralize the most difficult samples.

In figure 1b and 2b, the diagrams absorbance/time obtained for the determination of Pb and Cd in a cocoa liquor mineralized with the HPA apparatus are presented as examples. The severe diminution of the background absorptions versus the one of the figure 1a and 2a demonstrates the efficiency of the HPA mineralization.

The results for the analysis of Pb and Cd in standard samples are presented in table 2, whereas the results for the cocoa products are given in table 3. Each sample has been mineralized 6 times and the values represent the averages.

Table 2. Analytical results for Pb and Cd in reference materials

Reference material	Metal content in ppm			
	Pb		Cd	
	certified	analyzed	certified	analyzed
NBS-SRM 1577 Bovine liver	0.34 ± 0.08	0.38 ± 0.04	0.27 ± 0.04	0.30 ± 0.04
NBS-SRM 1568 Rice flour	0.045 ± 0.010	0.054 ± 0.010	0.029 ± 0.004	0.030 ± 0.005
BCR-RM No. 63 Natural skim milk powder	0.104 ± 0.003	0.104 ± 0.010	0.003 ± 0.001	Tr*
BCR-RM No. 150 Low spiked skim milk powder	1.00 ± 0.04	1.02 ± 0.03	0.022 ± 0.0014	0.022 ± 0.003
BCR-RM No. 151 High spiked skim milk powder	2.002 ± 0.026	2.06 ± 0.10	0.101 ± 0.008	0.110 ± 0.010

* Tr = 0.002 – 0.005 ppm Cd.

By studying the results obtained for the standards, we can observe that they correspond indeed to the given certified values. This proved that there are no losses by volatilization and the contaminations are avoided.

To further test the procedure, a whole milk powder was chosen with a Pb and Cd content below the detection limits of 10 ppb Pb and 2 ppb Cd. Recovery trials with this milk powder gave relative recoveries better than 95% (table 4) by spiking with Pb and Cd standard solutions before mineralization.

Among the most difficult samples with high fat content, cocoa liquor (55% cocoa butter) was given to be analyzed for Cd content by neutron activation in an external laboratory. The obtained result of 0.060 ± 0.003 ppm was in good agreement with our result of 0.055 ± 0.002 ppm. Likewise, the milk chocolate 2 was analyzed for the Cd content by AAS in an external laboratory. They found 0.007 ppm which is also in very good agreement with our result of 0.008 ± 0.002 ppm.

Table 3. Analytical results for Pb and Cd in some cocoa products

Product	Metal content in ppm	
	Pb	Cd
Cocoa liquor	0.035 ± 0.015	0.055 ± 0.002
Cocoa powder 1	0.230 ± 0.010	0.113 ± 0.005
Cocoa powder 2	0.140 ± 0.015	0.215 ± 0.008
Dark chocolate coating	0.030 ± 0.015	0.052 ± 0.005
Dark chocolate	0.034 ± 0.012	0.200 ± 0.020
Milk chocolate 1	0.060 ± 0.010	0.022 ± 0.004
Milk chocolate 2	0.030 ± 0.015	0.008 ± 0.002

Table 4. The relative recoveries of Pb and Cd for a spiked whole milk powder

Element	Quantity (ng)		Relative recovery (percent)
	Added	Found	
Pb	50	49.1	98.2
	100	98.5	98.5
	200	198.6	99.3
Cd	10	9.5	95
	25	24.3	97.2
	50	51.0	102

After studying the results of table 3, particularly the standard deviation values calculated from six analyses of the same sample, the precision can be judged as good, for concentrations exceeding 0.05 ppm for Pb and 0.01 ppm for Cd. These limits are low enough for routine survey of the Pb and Cd content in cocoa products. So, it is not justified to spend more efforts to improve our method to determine lower contents.

Furthermore, the obtained results on various chocolate samples show the expected variation for Pb and Cd content. These variations are due to the different origin of the cocoa beans (14–16). For instance, it is known that cocoa from South America contains generally more Cd than that from Africa. Attention must be drawn on the fact that the analyzed finished products were not made with the examined raw material described in table 3.

Conclusion

The wet digestion method with HNO₃ using the HPA is actually one of the best solutions for a complete mineralization of the products with high fat content. It may be highly trusted for the analysis of raw materials and finished products of the chocolate industry. Thanks to these results, we shall be able to build a data bank which will help us, for this category of products, to recognize a contamination going beyond the usual natural variation of the trace elements contents.

A large number of analyses are planned using the HPA procedure to study the variations of the Pb and Cd content in cocoa beans from different origins. Other raw materials and finished products will also be analyzed. The range of the analyzed elements will also be extended.

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Summary

The present work describes the successful use of the High Pressure Asher (HPA) mineralization device for the very difficult mineralization of materials with high fat content such as cocoa liquor, cocoa powder and chocolates.

First the Pb and Cd content in several certified standard materials were analyzed by electrothermal atomic absorption spectrometry after mineralization with the HPA. The obtained results are in good agreement with the certified ones. Recovery trials by spiking standard solutions to a whole milk powder before mineralization gave also relative recoveries better than 95%. The results for the Pb and Cd content in cocoa products showed a good reproducibility up to 0.05 ppm Pb and 0.01 ppm Cd.

Zusammenfassung

In der vorliegenden Arbeit wird die erfolgreiche Anwendung des Hochdruckveraschers HPA für die sehr schwierige Mineralisierung von Produkten mit hohem Fettgehalt wie Kakaomasse, Kakaopulver und Schokoladen beschrieben.

Vorerst wurde der Pb- und Cd-Gehalt in verschiedenen Referenzmaterialien, nach dem Druckaufschluss mit dem HPA, mittels elektrothermischer Atomabsorptionspektrometrie (ET-AAS) bestimmt. Die Resultate stimmten mit den vorgegebenen Werten gut überein. Wiederfindungsversuche, bei Zugabe von Standardlösungen zu einem Vollmilchpulver vor Mineralisierung, führten ebenfalls zu guten relativen Wiederfindungen von mehr als 95%. Die Resultate für den Pb- und Cd-Gehalt in Kakaoprodukten ergeben gute Reproduzierbarkeit bis zu 0,05 ppm Pb und 0,01 ppm Cd.

Résumé

Ce travail présente l'utilisation d'un four à haute pression spécial (HPA) permettant de pouvoir minéraliser de manière effective des produits contenant beaucoup de graisse, tels que masse de cacao, poudre de cacao et chocolats.

D'abord, les teneurs en Pb et Cd ont été déterminées dans des matériaux de référence à l'aide de la spectrophotométrie d'absorption atomique électrothermique (ET-AAS) après minéralisation par l'HPA. Les résultats alors obtenus concordent bien avec ceux indiqués par les certificats. Les essais de recouvrement effectués sur une poudre de lait, à laquelle des ajouts connus de Pb et Cd ont été effectués avant la minéralisation, ont donné des valeurs supérieures à 95%. Enfin, les analyses répétées de produits cacaotés ont montré une bonne reproductibilité pour des concentrations supérieures à 0,05 ppm de Pb et 0,01 ppm de Cd.

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