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İSTANBUL - TURKEY

ÇNAEM-R-177

THE INFLUENCE OF HEAT TREATMENT ON THE MERCURY CONTENT OF FISH FLESH

Meriç Alkan and Sevim Okar

P.K. 1, Hava Alanı, İstanbul, Turkey

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A B S T R A C T

The extent of mercury loss from fish flesh by heat treatment (during cooking) was investigated. The results of these experiments verified that the fish containing mercury should only be allowed to human consumption with special health consideration since the mercury loss due to even rather drastic cooking conditions, is about 50%.

The amount of mercury was determined by neutron activation analysis based on ^{203}Hg isotope. The radiochemical separation of mercury was performed by using iodinated resin. The efficiency of this separation was compared with that of the precipitation method of mercury as copperethylenediamine mercury iodide complex. No gold could be detected in the spectrum of copperethylenediamine mercury iodide complex whereas the contribution of gold activity to the 0.279 MeV peak of ^{203}Hg which was retained on iodinated resin could not be considered negligible. Therefore; when the mercury in any matrix in which gold also likely to be present, is determined by neutron activation analysis using iodinated resin, the contribution of gold should be taken into consideration or the 0.279 MeV peak activity of ^{203}Hg should be counted after complete decay of ^{198}Au.

Ö Z E T

PİŞİRMENİN BALIK ETİNDEKİ CIVA MİKTARINA ETKİSİ

Balık etinin ihtiva ettiği civa miktarında, ısı işlemi (pişirme) sırasında ne oranda bir eksilme olduğu incelenmiştir. Bu deneylerin sonuçları yüksek sıcaklıklardaki pişirme koşullarında (150-170°C) bile cıvanın ancak % 50 oranında eksildiğini göstermiştir. Cıva ihtiva eden balıkların tüketiminde insan sağlığı yönünden bu hususun göz önüne alınması gerekmektedir.

Cıva miktarı, Hg-203 izotopuna dayanan nötron aktivasyon analizi yöntemi ile tayin edilmiştir. Cıvanın radyokimyasal ayrımı, iyotlandırılmış reçineler kullanılarak yapılmıştır. Bu ayırmanın etkinliği cıvanın, bakıretilendiamin iyodür kompleksi halinde çöktürülmesi yönteminin ile karşılaştırılmıştır. Bakıretilendiamin cıva iyodür kompleksinin gamaspektrumunda altın görülmemiştir. İyotlandırılmış reçine üzerinde ayırmada ise Hg-203 izotopuna ait 0.279 MeV peak aktivitesine Au-198 izotopunun aktivitesinin katkısı saptanmıştır. Bu nedenle, altının da mevcut olduğu bir ortamda nötron aktivasyon analizi yöntemi ile ve iyotlandırılmış reçineler kullanılarak civa tayin edilecekse, Au-198 izotopunun katkısının göz önüne alınması veya Hg-203'ün 0.279 MeV peak aktivitesinin, Au-198 in tamamen bozunmasından sonra ölçülmesi gerekmektedir.

C O N T E N T S

THE INFLUENCE OF HEAT TREATMENT ON THE MERCURY CONTENT OF FISH FLESH

Meriç Alkan and Sevim Okar

I. I N T R O D U C T I O N

The determination of mercury content of fish flesh has gained wide interest in recent years from human health point of view. There are numerous methods for the determination of mercury in fish, such as atomic absorption spectrometry, neutron activation analysis, spectrophotometric and chromatographic methods. The main common problem in all of these methods in the loss of mercury during sample handling. It is known that the loss of mercury can be overcomed or at least decreased down to a negligible level by carrying out the necessary operations at low temperatures and in closed systems. Without doubt, the most important factor affecting the volatility of mercury, thus causing the loss of the element from fish flesh, is heat. Most of the fish meals for human consumption require heat in their preparation. The fish which are considered unfit for human consumption due to their high mercury content, could be consumed only if sufficient amount of mercury loss occurs (during cooking). Therefore; it seemed worthwhile to find out the extent of mercury loss from fish flesh by heat treatment.

In the present work the amount of mercury was determined by neutron activation analysis based on ^{203}Hg isotope. The radiochemical separation of mercury was performed by using iodinated resin. The efficiency of this separation was compared with that of the precipitation method of mercury as copperethylenediamine mercury iodide complex which was previously applied in our laboratory.

II. E X P E R I M E N T S

Preparation and irradiation of samples: Samples of 1-2 g homogenized fish flesh were weighed in quartz ampoules. Some of these samples were kept in an oven at 150-180°C for 20 minutes in order to simulate the cooking procedure. Known amounts of

$Hg_2(NO_3)_2 \cdot 2H_2O$ in identical quartz ampoules were used as standards. Fish samples (cooked and raw) and the mercury standards, all sealed in quartz ampoules, were irradiated in TR-1 reactor in a flux of $1.2 \times 10^{12} n.cm^{-2}.sec^{-1}$ for 7 hours and then cooled for about 4-5 days.

At the end of cooling period all quartz ampoules were washed in 1N HNO_3, rinsed with water and frozen in liquid nitrogen. The ampoules were broken and the fish material together with broken quartz pieces were transferred to 50 ml digestion flasks.

750 µg of Hg-carrier and 3 ml of a mixture of HNO_3/H_2SO_4 (5:1) were added to the samples. The mixture was heated under reflux for 30 minutes in order to wet-ash the samples. The solution was diluted with a few milliliters of water and filtered. Adjusting the pH of the filtrate to 2-2.5, the aqueous solution was passed through an iodinated resin column prepared as described by Heurtebise [1]. The column was washed with 2-3 ml 10% NaBr-solution and finally with distilled water. The resin was transferred to a glass counting disk of 2.5 cm diameter and dried at room temperature. The standard mercury was processed in the same manner as the samples.

Another group of irradiated fish samples and a mercury standard were wet-ashed in identical conditions by adding 10 mg of mercury as carrier. The wet-ashed material was processed according to a method described by H. Smith [2] in order to determine the amount of mercury as copperethylenediamine mercury iodide complex.

A 400 channel gamma spectrometer equipped with a 3in.x 3in. NaI(Tl) crystal was used for counting the 0.279 MeV peak of ^{203}Hg activity.

III. R E S U L T S A N D D I S C U S S I O N

The results of mercury contents of several kinds of fish previously analyzed in our laboratory by neutron activation analysis are given in Table I.

Table I. Mercury Content of Raw Fish Flesh[a]

Variety of Fish	Hg-content (/ug/g fish, wet-weight)
Monkfish	0.43
Sturgeon	0.30
Turbot	0.41
Anchovy	0.20
Thunny fish	0.35
Monkfish (present work)[b]	0.41

[a]Determined as copperethylenediamine mercury iodide complex.
[b]Determined as copperethylenediamine mercury iodide complex and by retention on iodinated resin.
(Each value is the mean of at least 3 determinations.)

The efficiencies of the two separation methods for mercury (i.e. the use of iodinated resin and the precipitation as copperethylenediamine mercury iodide) were compared with each other by studying the gamma spectra of separated ^{203}Hg. In Fig. I a, the shape of the spectrum of copperethylenediamine mercury iodide complex proves the radiochemical purity of the mercury separated [3].

The use of iodinated resin for mercury determination in fish by neutron activation analysis based on ^{197}Hg isotope has previously been applied by Lubkowitz et al. [4]. Although in their work ^{197}Hg separated by this method was found sufficiently pure to be counted, the same separation technique applied to our fish samples, did not achieve to the same radiochemical purity. As can be seen in Fig. I b, the peak at 0.411 MeV energy range indicates the presence of ^{198}Au which was retained on the resin together with mercury.

Therefore; when the mercury in any matrix in which gold also is likely to be present, is determined by this method, the contribution of gold should be taken into consideration or the

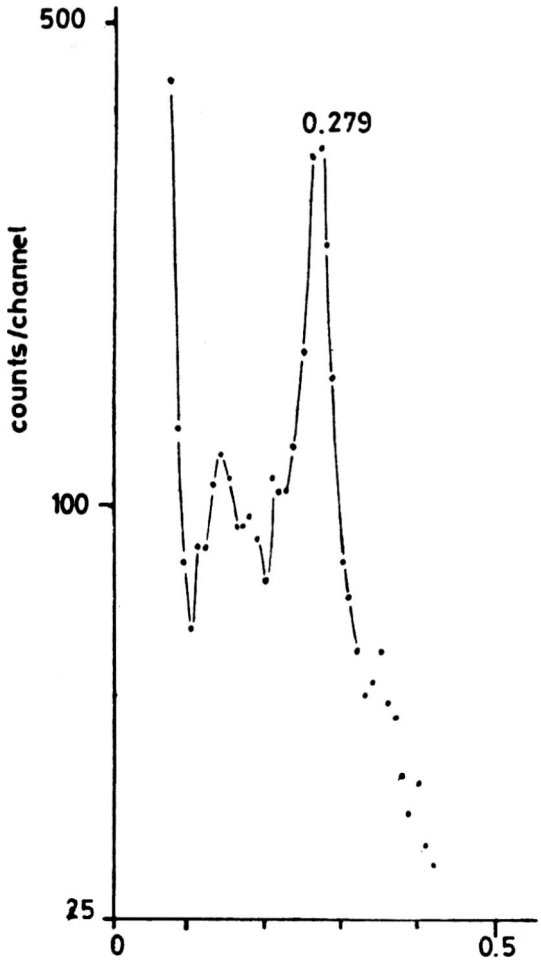

Fig.1 a. Gamma ray spectra of mercury separated from fish flesh by precipitation as copperethylenediamine mercury iodide complex.

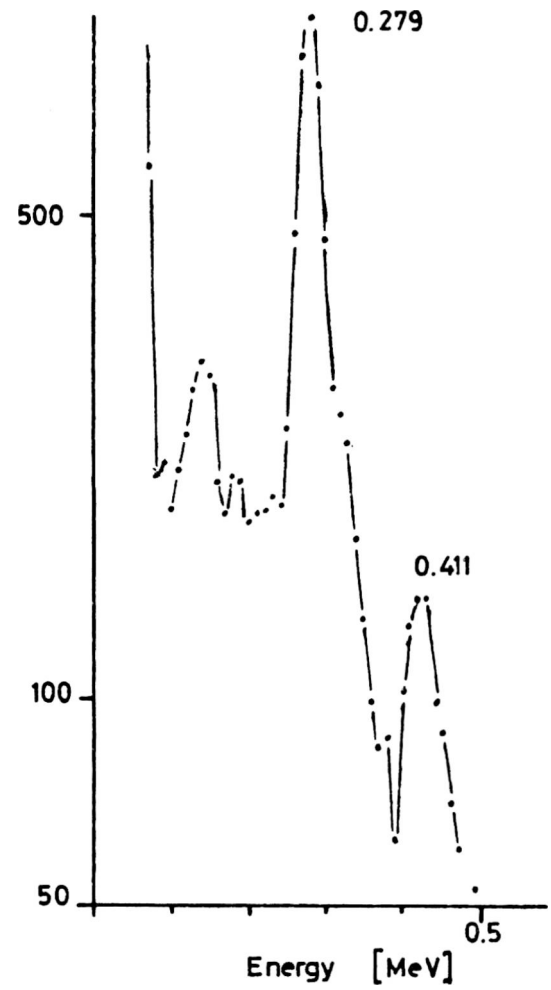

Fig.2 b. Gamma ray spectra of mercury separated from fish flesh by retention on iodinated resin.

0.279 MeV peak activity of ^{203}Hg should be counted after complete decay of ^{198}Au.

Despite of its lower decontamination factor which can be obtained in only one step, the use of iodinated resin is superior to the previous precipitation method for its speed and simplicity.

Due to its relatively high mercury content, monkfish was used for the investigation of the influence of heat treatment (cooking) on mercury loss of fish flesh. The results of the experiments are given in Table II.

Table II. The influence of Heat Treatment on Mercury Content of Fish Flesh[a]

Sample	Hg-content (µg/g fish, wet-weight)
Monkfish, raw	0.41
Monkfish, cooked at 150-180°C for 20 min.	0.21
Mercury lost %50	

[a]Determined by retention on iodinated resin. (Each value is the mean of at least 10 determinations).

The upper limits to the amount of mercury in fish used for consumption set by various government agencies, are usually in the range of 0.5-1.0 ppm (0.5 ppm in Canada and USA, 0.7 ppm in Italy and 1.0 ppm in Sweden).

In conclusion, it can be said that the results of our experiments verified the fact that the fish containing mercury, should only be allowed to human consumption with special health consideration since the mercury loss due to even rather drastic cooking conditions, is about 50%.

REFERENCES

1. H. Smith, Anal. Chem., 35, 635 (1963)
2. M. Heurtebise and W.J. Ross, Anal. Chem., 44, 596 (1972)
3. R.L. Heath, "Scintillation Spectrometry, Gamma-Ray Spectrum Catalog" USAEC Rep. IDO-16408.
4. J.A. Lubkowitz, F. Montoloy and M. Heurtebise, Radiotracer Studies of Chemical Residues in Food and Agriculture, Panel Proceedings Series, IAEA Vienna, 1972, p.77.