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Comparison of the spectrophotometric and the ion chromatographic method for the estimation of hexavalent chromium in organic matrices

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Abstract

Spectrophometric method involving diphenylcarbazide (EPA method 7196A) and the ion chromatographic method (EPA method 7199) have been used for the determination of hexavalent chromium [Cr(VI)] in different body parts of chicken and in yolk and albumen of eggs of Bangladesh. Ion chromatographic method has been found to provide higher amounts of Cr(VI) than the spectrophotometric method in most cases. This is not unexpected, as Cr (VI) can be reduced to Cr(III) during the process of measurement by the reducing agents present in the matrix. Chicken parts/eggs are known to contain a substantial amount of reducing material. In the EPA method 7199, a guard column removes some of these reductive species. Methods 7196 and 7199 which were originally recommended by the USEPA for analysis of soil samples do not seem to work very well with such organic samples containing reducing species. More work is needed to develop a suitable method for such systems.

INTRODUCTION

Chrome tanning being the most common process practiced in the Hazaribag tanning industries of Dhaka, chromiun is entering different food items of Bangladesh through the use of solid tannery waste as the principal component of poultry feed, fish feed and fertilizers [1-2]. In view of the gravity of the situation, the national media like The Daily Star [3] and The Prothom Alo [4] have run articles on the subject. 'Cancer-producing chemical present in fish and chicken' was the title of a report published as recently as April 7, 2014 in The Daily Manab Zamin [5]. The situation with other countries of the sub-continent, namely, India and Pakistan, is not very different. P N Sudha [6] in her article entitled, "Are we eating chrome chicken", has described the transfer of Cr from leather waste to chicken through poultry feed in the Tamil Nadu state of India, which is home to some 900 tanneries. Mahmud et al [7] have found high concentrations of chromium in different body parts of chicken collected from a Lahore market in Pakistan.

Toxicity of chromium depends on its valence state. Whereas trace amount of Cr(III) is useful for health, Cr(VI) is highly toxic and can cause mutation, cancer and cell damage [8]. Thus, from the point of view of public health, measurement of Cr(VI) is more pertinent than that of total chromium, which has been done by most of the previous workers. Using the USEPA method, 3060A of alkaline digestion [9], followed by spectrophotometric measurement of the colored complex that is formed on addition of 1, 5- diphenylcarbazide (EPA method 7196A) [10], Mazumder, Hasan & Rahman [11] have found hexavalent chromium in leather waste, poultry feed, and even in some chicken livers of Dhaka city. Very recently, we have found the presence of Cr(VI) in liver, gizzard and flesh portions of chickens collected from different parts of Bangladesh [12]. Even the yolk and albumen of eggs have been found to contain small amounts of Cr(VI).

In the present paper we have compared the spectrophotometric method with a more sensitive and sophisticated one, namely, the ion chromatographic method and the results have been discussed.

MATERIALS AND METHODS

A. Chemicals

Analytical grade chemicals were obtained from E Merck, Germany and used without further purification. Methanol was of HPLC grade.

B. Apparatus

Shimadzu UV-1700 model double-beam spectrophotometer was used for absorbance measurements. pH was adjusted with a pH meter, model Sension ™ 156 of Hach, USA. Ion chromatograph was from Shimadzu, Japan. Digestion of samples was carried out in an automatic digester, model ETHOSD microwave labstation of Milestone.

C. Calibration of the instruments

Both the spectrophotometer and the ion chromatograph were calibrated with respect to standard solutions of potassium dichromate. Graphs of absorbance versus concentration were straight lines with the value of R^2 being greater than 0.999. Sandell's sensitivity and detection limit were found to be 1.2 ppb cm^{-2} and 1.9 ppb respectively for the spectrophotometer. For the ion chromatograph the graph of concentration versus area was a straight line with R-values being 0.999 and 0.999. Detection limit for the instrument was 0.15 ppb.

D. Sample Analysis

After following an alkaline digestion procedure (USEPA Method 3060A) [9], the sample was analyzed according to the procedure, USEPA Method 7196A, the details of which have been described elsewhere [11]. In the other method, EPA Method 7199 [13], ion chromatography was used to separate chromate ion from other species by passing through a chromatographic column and the chromate ion was then analyzed in the same way as in the method 7196A. The details of the procedure have been described in reference [12].

RESULTS AND DISCUSSION

For spectrophotometry at least 5 absorbance readings were taken and Excel program was used to calculate the mean and the standard deviation. Typical chromatograms have been shown in Fig. 1 and 2 for chicken liver and egg yolk respectively.

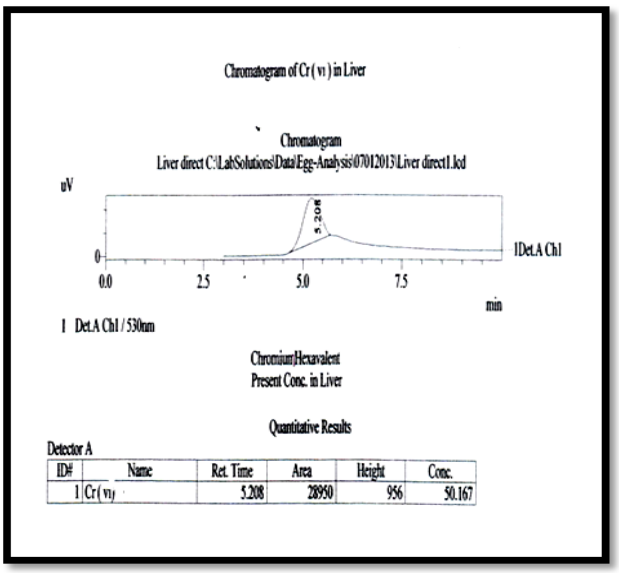

Fig. 1. Ion chromatography peak for liver

Spectrophotometry and ion chromatography have been used to measure Cr(VI) in the same samples and the results are shown in Table 1. It would be seen that except for a sample of albumen all the results are higher for ion chromatography than for spectrophotometry.

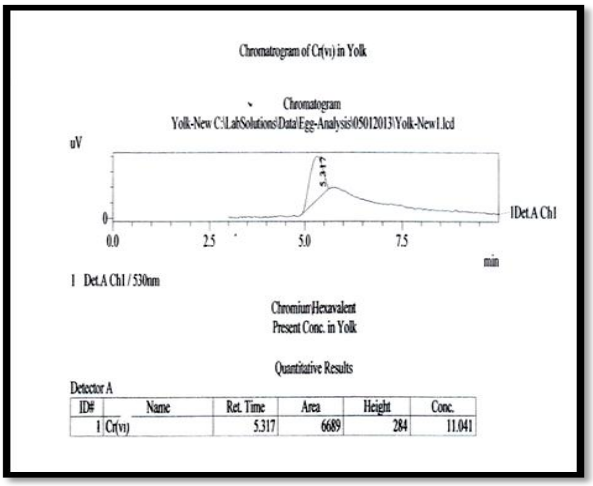

Fig. 2. Ion chromatography peak for yolk

Table 1. Comparison of spectrophotometric and ion chromatographic results

Sam. No.	Body Parts/ Eggs	Amount of Cr (VI) (mg/kg) by Spectrophotometry	Amount of Cr (VI) (mg/kg) by IC
1	Liver	1.008 ± 0.12	3.456
2	Gizzard	0.646 ± 0.049	0.904
3	Albumen	0.415 ± 0.306	0.497
4	Albumen	1.03 ± 0.33	0.938
5	Yolk	0.191 ± 0.03	0.36

This pattern is in agreement with literature values. The New Jersey Chromium Workgroup has tried to explain this behavior [14].

In order to understand these results we have to go back to basic chemistry of chromium. As is well known, chromium can exist in oxidation states ranging from 0 to +6, the +3 state being the most stable. The standard reduction potential for Cr^{6+} to Cr^{3+} is very high in acid medium (1.33 V), which means that hexavalent chromium is easily converted into trivalent state in an acid medium if there is a suitable reducing state available. This is the reason why EPA has suggested maintaining an alkaline pH during the digestion of the samples. Unfortunately pH of ~ 2.0 is required for the formation of the colored complex with 1, 5-diphenylcarbazide. Thus the medium becomes highly acidic and the possibility of some Cr(VI) being reduced cannot be ruled out. In the case of ion chromatography the digested solution is passed through a guard column before being led into the anion exchange separator column. The guard column removes some of the organics including organic reducing agents. Higher values of Cr(VI) as obtained here can thus be explained.

Inter conversion of Cr(VI) and Cr(III) makes the spiking recovery difficult. Considering the inherent difficulties in controlling the conditions for preventing inter conversion, the EPA has allowed wide margin in the percentage of spiking recovery [14]. In the present case spiking recovery was negligible. The reason may lie in the nature of the matrices here, which are organic as opposed to soil samples for which these methods (7196A & 7199) were developed. It seems that even the guard column could not remove the organic reducing agents effectively.

CONCLUSION

It appears that the EPA methods 7196A and 7199 are not completely satisfactory for the measurement of hexavalent chromium [Cr(VI)] in organic samples like chicken and egg. Either, these methods have to be modified or new methods have to be developed for such systems.

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