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EXPLANATION OF THE SHAPE OF CALIBRATION GRAPHS OBTAINED FOR MERCURY, ZINC AND COPPER IN STREAM WATER SAMPLES

BY

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ملخص

لقد عينت اشكال قياسية لكل من عناصر الزئبق، الزنك والنحاس في مياه الجداول قبل وبعد تعريضها لقوة الطرد المركزي. وتم تفسير الاشكال القياسية الناتجة بناء على نظريتين، واحدة ترجع الشكل الناتج الى تاثير امتزاز ايونات العناصر المضافة على الحبيبات العلقة في الماء وعلى سطح الإناء المستعمل لحفظ العينات. أما النظرية الثانية فترجع الشكل الناتج الى تاثير تداخل مواد كيماوية موجودة في الماء مع القراءات الناتجة عن تحليل العناصر المضافة. هذا وقورنت النظريتان مع بعضهما من حيث نقاط القوة والضعف بينهما. كما تمت دراسة تاثير الزمن على الاشكال القياسية للعناصر.

ABSTRACT

Calibration graphs have been obtained for mercury, zinc and copper ions using buffered (pH 7.4) stream water and centrifuged stream water samples. Two hypothesis explaining the shape of the obtained calibration graphs have been suggested; one refers the shape to the adsorption of trace elements on the suspended particles and on the container surfaces, the other hypotheses refers the shape of calibration graphs to the presence of chemical interference. The strength of the two hypotheses has been compared. The effect of time on the shape of the calibration graphs has also been investigated.

INTRODUCTION

Adsorption on the suspended particles of natural water has been studied by several authors [1-8]. A large portion of trace elements has been proved to be adsorbed on suspended particles. Adsorption of trace elements on container surfaces has also been found substantial [9,10] .

Calibration curves are usually used as evaluation methods for translating experimental values (e.g. absorbance readings in AAS) into concentration value. However, a difficulty usually arises in natural water samples where curved, and not linear, calibration graphs are usually obtained [1,11,12].

The aim of this paper is to study the relation between the curved shape of calibration graphs obtained for the elements copper, mercury and zinc in stream samples and the adsorption of these elements on the suspended particles present in the stream water samples and on the container surfaces.

EXPERIMENTAL

Apparatus:

A Pye Unicam Atomic Absorption Spectrometer-Model SP 192 was used for determining metal ion concentrations in solution. An acetylene-air flame was used, the optimum conditions used for the analysis of metals were similar to those recommended by the manufacturers of the instrument.

Centrifugation was carried on using Sorvall RC-5B Refrigerated Superspeed Centrifuge, supplied by Du Pont Company, Newtown, CT. Centrifugation was always carried out at 4°C using 6000 rpm for 30 min. This amount of centrifugation represents the maximum efficiency for separting suspended particles from natural water samples [13].

Reagents:

All reagents used were of ANALAR quality. Stock solutions of metal ions were prepared as recommended by the manufacturers of the AAS instrument.

Sampling:

Natural water samples were collected from an unpolluted stream-water (El-Badan) close to the city of Nablus. Samples were found to give zero absorbances when checked for the three elements studied here. Fresh natural water samples were used as solvents for establishing the calibration graphs shown in this work. Clean polythene bottles were used for sampling purposes.

RESULTS AND DISCUSSION

Shape of Calibration Graphs:

Calibration graphs were obtained for mercury, zinc and copper using buffered (pH 7.4 using acetate buffer) stream water and buffered centrifuged stream water. The results obtained (Figs.1,2,3&4) show the following :-

1. Calibration graphs obtained for the elements Hg, Zn and Cu show curvature in the low concentration ranges.

2. Calibration graphs are linear in the high concentration ranges.

3. Centrifugation affects the shape of the calibration graphs. Calibration graphs obtained using the lower half of centrifuged stream water samples show more distinct curvature and lower absorbance values than calibration graphs obtained using uncentrifuged stream water samples.

4. Calibration graphs obtained using the upper half of centrifuged stream water samples do not show curvature and show higher absorbance values than the calibration graphs obtained using uncentrifuged stream water samples.

The above results can be explained with reference to the effect of adsorption of metal ions onto the suspended particles present in stream water and adsorption of these ions also on the container surfaces.

At low concentrations, most of the ions added become adsorbed onto the suspended particles and on the container surfaces. This adsorption leaves only a small part of the metal ions to contribute to the absorbance value; this results in a considerable deviation from the absorbance expected if no adsorption had occurred.

At higher concentrations than above, a smaller fraction of metal ions is adsorbed, and thus, the deviation of the experimental results from the results expected, if no adsorption had occurred, is less than at lower concentrations.

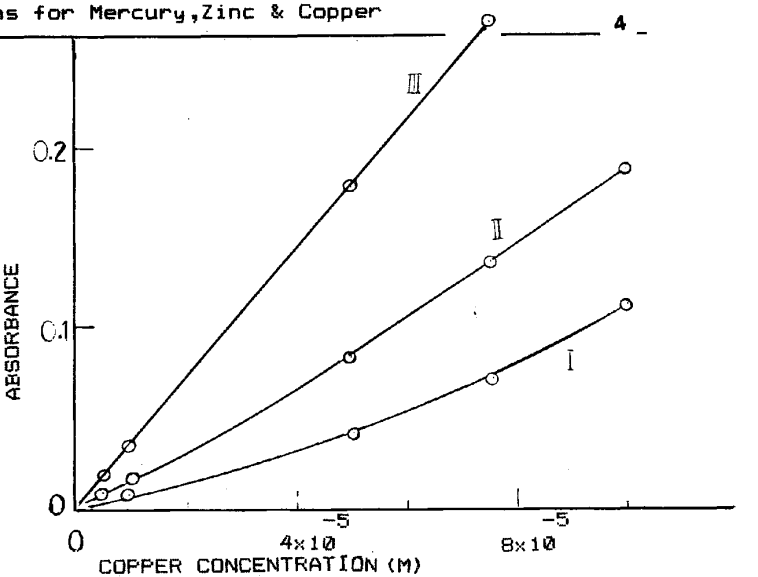

Fig. 1. Calibration graphs for copper in the low concentration range:
I . Centrifuged stream water - lower half.
II . Uncentrifuged stream water.
III. Centrifuged stream water-upper half.

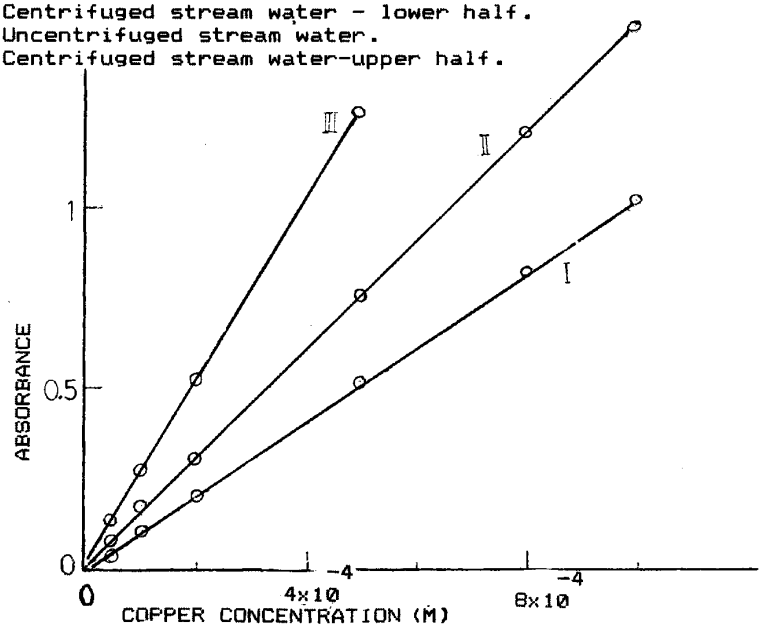

Fig. 2. Calibration graphs for Copper in the high concentration range:
I . Centrifuged stream water - lower half.
II . Uncentrifuged stream water.
III. Centrifuged stream water - upper half.

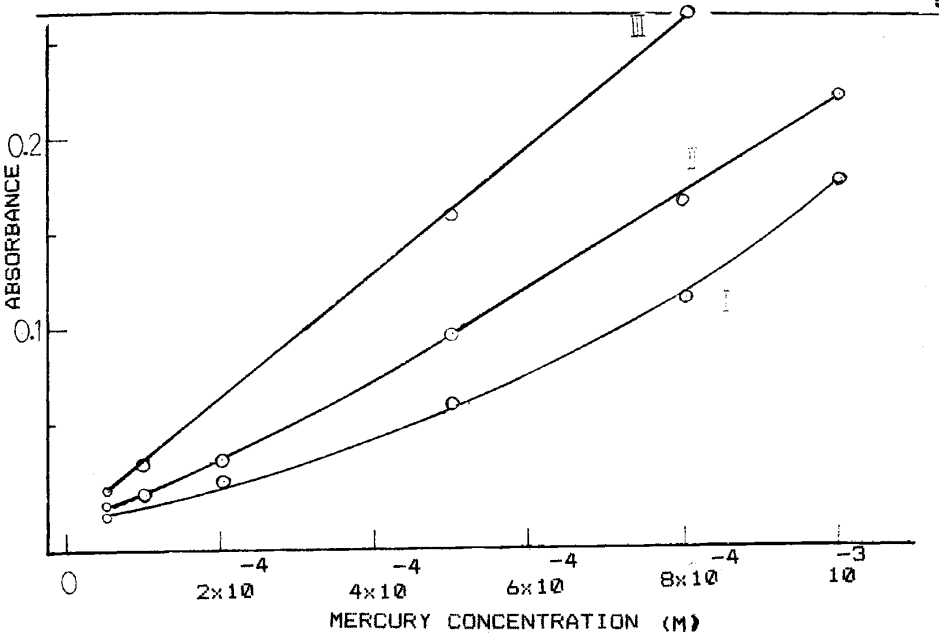

Fig. 3. Calibration graphs for mercury:
I . Centrifuged stream water - lower half.
II . Uncentrifuged stream water.
III. Centrifuged stream water - upper half.

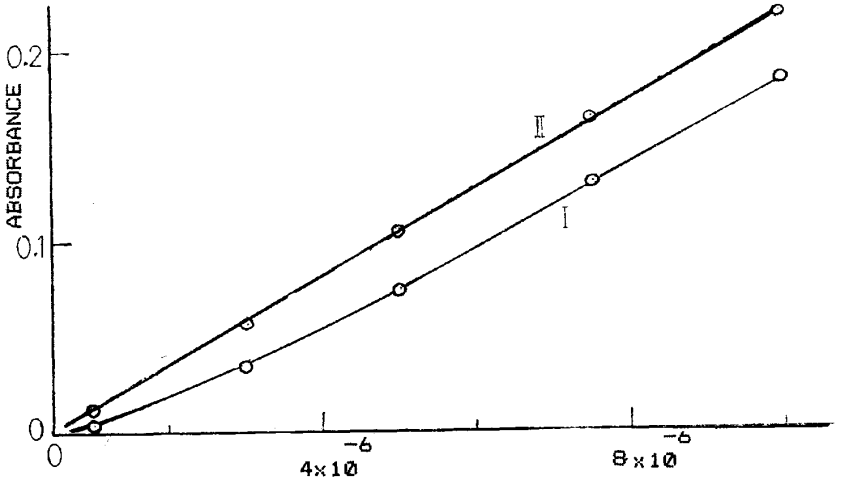

Fig. 4. Calibration graphs for zinc:
I . Centrifuged stream water - lower half.
II . Centrifuged stream water - upper half.

In AAS, a straight line calibration graph is aniticipated. The effect of adsorption is to give low results at low concentrations and, thus, causes curvature at low concentrations.

The difference between the value of absorbance obtained in centrifuged and uncentrifuged natural water samples is due to removal of some of the particles from the stream water. This removal results in decreasing the number of adsorption sites and thus, a larger part of the metal ions added is contributing to the absorbance value. Sufficient centrifugation to separate all suspended particles results in the disappearance of curvature from calibration graphs obtained in the clear half of the centrifuged stream water samples (c.f. Fig$. 1-4) .

In addition to the effect of adsorption another possible hypothesis may be suggested to explain the curvature in the calibration graphs at low concentrations of metal ions. This hypothesis relies on the possible presence of minute quantities of chemical entities in stream water causing chemical interference. These entities might form compounds with the added metal ions having higher atomization temperature; this prevents metal ions from contributing to the absorbance value obtained. At high metal ion concentrations, these chemical entities would be completely consumed resulting in a linear calibration graph.

Effect of Time on the Shape of Calibration Graphs:

The absorbance of a solution of copper in stream water has been found to vary with time. This variation has been followed experimentally and the rersults of this variation are shown in Fig. 5. These results show a rapid decrease of the absorbance value (indicating a rapid decrease of the concentration of copper in solution) in the first few minutes and then this decrease continues slowly for a long time. This trend is very similar to the trend resulting from the effect of adsorption of trace elements on the suspended particles [15-17] and on container surfaces [10]. This might suggest that the effect of time shown here is also due to adsorption of copper on the suspended particles of stream water and on the container surfaces.

Calibration graphs obtained for copper in stream water after various waiting times showed a systematic decrease in the absorbance values and in the slope of calibration graphs with increasing time (c.f. Fig. 6) .

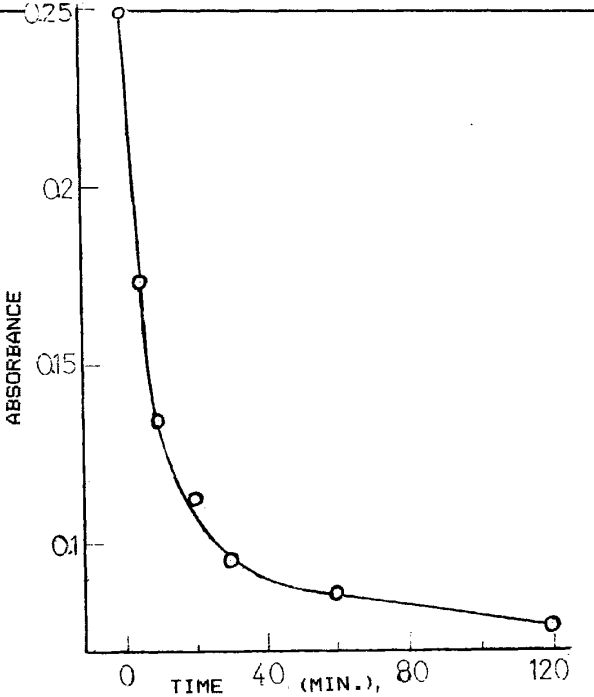

Fig. 5. The effect of time on the absorbance values measured for a 5X10 M copper solution in stream water.

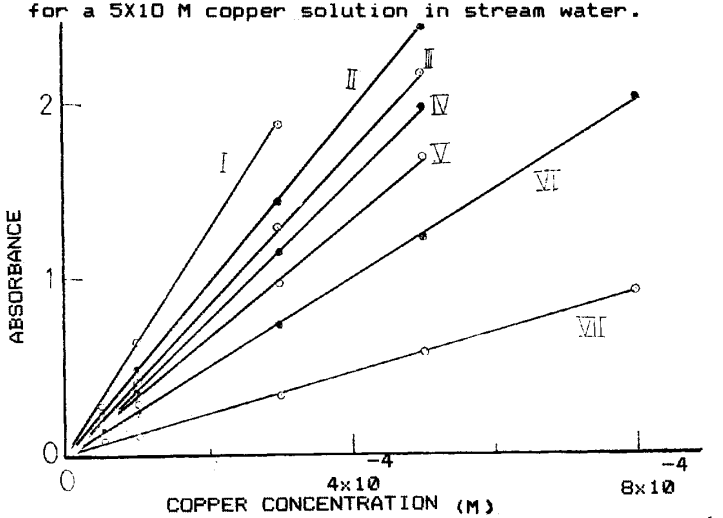

Fig.6.The effect of time on calibration graphs for copper in stream water: I. 0 min II. 5 min. III. 10 min IV. 30 min V . 60 min VI 2 hr VII. 24 hr.

Comparison Between the Hypothesis of Adsorption and the Hypothesis of Chemical Interference:

Comparing the effect of adsorption with the effect of interferences as explanations for the shape of calipration graphs it can be concluded that the adsorption hypothesis fits more on the present results; the reasons are:

1. The absorbance difference between calibration curves obtained from centrifuged and uncentrifuged samples can be easily explained via the adsorption hypothesis because centrifugatin separates a part of the suspended particles and therefore less fraction of the added metal ions is left free in solution of the lower half of the centrifuged samples and thus lower absorbance values are obtained in the lower half of the centrifuged stream water samples than in the uncentrifuged water samples or in the upper half of the centrifuged sample. Trying to explain the effect of centrifugation relying on the possible presence of chemical interference is not successful because centrifugation is not expected to affect the chemical interference which is caused by dissolved chemicals in water.

2. It has been proved, in the literature, that adsorption was the cause of similar shaped calibration graphs obtained for lead, cadmium and copper [1,14] in natural water samples. This proof was achieved via applying a theoretical equation derived for the adsorption process on the obtained experimental results.

3. The effect of time (discussed above) on the calibration graphs is conveniently explained as being due to the effect of adsorption.

CONCLUSIONS

The following conclusions can be drawn from the present results:-

1. Calibration graphs obtained for mercury, zinc and copper ions in stream-water and in centrifuged stream water show curvature in the low range concentration and become linear in the high range concentration.

2. Calibration graphs of mercury, zinc and copper obtained in centrifuged stream water (lower half) show lower absorbance values and those obtained in centrifuged stream water (upper half) show higher absorbance values than calibration graphs obtained in uncentrifuged stream water.

3. Curvature disappears from calibration graphs obtained in the upper half of the centrifuged stream water samples. Curvature becomes more distinct in the calibration graphs obtained from the lower half of centifuged stream water samples than in the calibration graphs obtained from uncentrifuged stream water samples.

4. Shape of calibration graphs can be explained via either the effect of adsorption on suspended particles and on container surfaces or the effect of chemical interferences. There are several indications that the adsorption hypothesis is the stronger one.

5. The absorbance of a concentration of metal ion in stream water decreases with time. The calibration graph obtained after a long waiting time shows less absorbance values and less slope than calibration graphs obtained after a shorter waiting time.

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