November 2006 Volume 1 Issue 4-6

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 1(4-6), 2006 [146-151]

A Photoacoustic Study On Chromium (VI) In Water

Corresponding Author

K.Ramachandran
School of Physics,
Madurai Kamaraj University, Madurai, (INDIA)
E-mail: thirumalchandran@g.mail.com

Received: 31st Augest, 2006
Accepted: 11th September, 2006

Web Publication Date : 14th November, 2006

Co-Authors

G.Krishna Bama[1], S.K.Ramakrishnan[2]
[1]Sri Meenakshi Government Arts College for women, Madurai,(INDIA).
[2]Department of Chemistry, Thiagarajar College, Madurai, (INDIA).

ABSTRACT

Photoacoustic study is carried out here to find the concentration of chromium(VI) in water. The results reveal that the present method can also be used as an additional tool to support the results of ion chromatography and chemi-luminescence.

KEYWORDS

Photoacoustics;
Chromium (VI);
Thermal diffusivity.

INTRODUCTION

Chromium contamination of surface and ground waters is a persisting problem in many countries. With regard to human health chromium (III) is a required nutrient with 50 to 200 μg per day recommended for adults[1]. On the contrary chromium (VI) is toxic and carcinogenic for the human body[2,3] leading to lung cancer, skin allergy and probably also to asthma and renal diseases. The US EPA recommended the maximum allowed dosage of Cr(VI) in drinking water is 0.96μmol^{-1}[4]. Hence the determination of chromium (VI)level in drinking water is a very important task because of the environmental impact, toxicity and bioavailability of chromium. At the turn of the millennium one requires compact, reliable, cheap and time-effective sensors for this measurement in liquids, capable of reaching the desired detection limits in each application without the need for large sample volumes[5]. The conventional techniques (e.g. liquid spectrophotometry), are mostly off-line as well as time and great-sample-volume consuming; the detection range is limited by the sample absorbance and in spectrophotometry this is usually between 0.01 and 2.

Ion-chromotography is one of the best methods for determination of ions in water samples when this is coupled with UV detection[6]. This is useful upto a limit of 0.1 μgL^{-1}. The deficiency here is, that the method is complex than direct methods. Similarly Stoyanova[7] had estimated the chromium(VI) concentration by catalytic process, where the reaction was followed spectrophotometrically by measuring the absorbance of the reaction product at 360nm.

By drawing a calibration graph for chromium (VI) upto 200 ng mL^{-1}, the concentration of Cr(VI) in any sample was found out. Still this method is complex.

So alternative techniques are being attempted to exactly find the concentration of Cr(VI) in water in a simple way. Photothermal (PT) methods have recently been identified for the above mentioned requirements. Among the various types of PT techniques the photoacoustic(PA) method is widely used for measurement of thermal and optical properties of liquids. Recently Lima et al.[8] have carried out PA measurements by open photoacoustic cell for the determination of chromium (VI) in water. They have also drawn a calibration graph connecting Cr (VI) concentration and normalized photothermal amplitude by which they could estimate the molar extinction coefficient comparable with optical spectrometry. Here presented a still simpler photoacoustic method to study the Cr (VI) concentration.

The principle of PA effect is based on the light-induced heat release and subsequent acoustic generation from a material when it is irradiated with modulated optical radiation. The dependence of PA signal on both the thermal and optical properties of the sample makes it a convenient method for the study of materials in different forms. The thermal diffusivity similar to thermal effusivity, is a unique thermal transport property of a material. In the present work the photoacoustic technique is used to measure the thermal diffusivity of chromium (VI)in water for various lower concentration. If a calibration graph connecting the thermal diffusivity and concentration is arrived, then the Cr(VI) in any water can be immediately found out.

Sample preparation

The samples of Cr(VI) contaminated water of different concentrations are prepared in the laboratory. The glass materials were first cleaned following the standard procedures. Then deionised-distilled water is taken and K_2CrO_4 is used to prepare a water sample with Cr(VI). A stock standard solution of 0.01 mol/lit Cr(VI) was prepared from potassium chromate by dissolving the stiochiometric of K_2CrO_4 in 100 ml of deionised water. The experiments were carried out with these solutions containing Cr (VI) in the range 0.009-0.001 mol /lit Regular chemical tests were carried out to confirm the presence of Cr (VI) in the water samples.

Ultrasonic measurements

Ultrasonic methods are being extensively used to study molecular interaction in pure liquids and liquid mixtures. From the knowledge of ultrasonic velocity and density of a liquid, various acoustical parameters such as adiabatic compressibility, molar volume, free volume, internal pressure etc. can be obtained. In general the excess thermodynamic functions such as excess compressibility, molar volume, enthalpy and Gibb's free energy are useful in understanding the nature of molecular interactions[9].

As the ultrasonic measurements are non invasive and proven techniques for such measurements these were also carried out here for the above chromium contaminated solutions. The ultrasonic velocities were measured using an ultrasonic interferometer of fixed frequency 2 MHz.

The resulting ultrasonic velocities measured with this technique are given in TABLE 1. The results indicate that such a low concentration of Cr(VI) cannot be determined efficiently by ultrasonics technique, as there is no change at all in the speed of sound in these water samples and the sonication also has no effect on the Cr(VI) ions.

UV-VIS absorption measurements

Cr (VI) has a strong uv-visible spectrum with a very large molar absorption co-efficient of 1550 mol^{-1} $dm^{-3}cm^{-1}$ at 350 nm[10]. In the present work UV-Visible absorption measurements were also observed for chromium (VI) concentration in the range of 0.04 - 0.5 $molL^{-1}$ and is given in TABLE 2, for the absorption. From UV-visible absorption no mode could be observed for Cr (VI) concentration below 0.04 mol L^{-1}, even though the mode at around 450 nm

The results of UV-Vis and ultrasonic measurements reveal that, these methods are not efficient tools for determining Cr(VI) in water for lower concentration to a level of μmol^{-1}, as such when they are used as independent tools.

Conventional PA theory in liquid

In liquids, the generation of acoustic waves is

Current Research Paper

TABLE 1: Ultrasonic velocity with Cr (VI) concentration

Molality(mole/lit)	Ultrasonic velocity m/s
0.5	1564±9
0.05	1504±9
0.01	1496±7
0.008	1500±8
0.007	1500±9

TABLE 2: UV-Vis for Cr^{6+} for different concentration for a particular absorption.

Molality in mol L^{-1}	Mode due to Cr^{6+} (nm)	Absorption (Intensity in arb.units)
0.5	491	1.405
0.4	490	1.352
0.3	488	1.249
0.2	485	1.071
0.1	480	0.642
0.07	478	0.472
0.06	477	0.228
0.04	442	0.111

generally due to two different mechanisms: optical absorption followed by thermal de-excitation, as in thermal expansion and liquid boiling, or non-thermal de-excitation, as in the case of photo chemical process and breakdown. In addition, optical non-absorption such as electrostriction and radiative pressure may also produce acoustic waves. The thermal elastic expansion mechanism is an interesting choice for material characterization and medical diagnosis for a variety of reasons. Firstly, it does not break or change the properties of the object under study. Secondly, it has a linear or a definite relationship with many of the physical parameters of diverse materials. Thirdly, it is non-destructive or non-invasive in application such as materials test and medical diagnosis. Therefore, photoacoustics which is based on thermal elastic expansion becomes an automatic choice.

Photoacoustic spectrometer

400 W Xe- lamp (Jobin Yvon) is used as the light source. The sample chromium (VI) water is placed in the PA cell and a microphone is placed very near to the sample. The PA cell here is unconventional in the sense that it is made up of glass of needle type with a diameter of 1mm and length of about 3cm with one end sealed. The liquid is injected into this needle shaped cell and sealed at the other end. This has to be placed in a glass funnel on the stem, which is designed as follows. A glass funnel is completely blackened inside by carbon black and the wider end is sealed with a concave watch glass. Along the funnel on one side a small hole of diameter of 1.5 mm is drilled. The sample tube now is inserted into this hole and sealed with paste. At the end of the stem of the funnel a microphone is inserted and closed. The whole compartment, the PA cell, should be airtight and soundproof. So extra care is taken in the design of the cell.

It is known that the amplitude of PA signal will increase when the dimension of the PA cell is decreased, but one should also monitor that no unwanted resonances take place. So, the dimension of the cell is very important. In general the amplitude of the PA signal will be very much weak compared to solids and so the PA cell should be designed carefully. To get the modulated light, a mechanical chopper (Model number PAR 650) is used with the source. The PA signal from the sample is fed to a lock in amplifier (Model Perkin Elmer 7225 DSP) and a digital storage oscilloscope (Gould 20 MHz systronics) The light is allowed to fall on the sample through a monochromator (Model Triax 180, Jobin Yvon). Before doing the actual experiments, the spectrum profile of Xenon lamp was studied for normalization. The complete picture of the present photoacoustic spectrometer is shown in figure 1.

Thermal diffusivity

In general depth profile analysis will be carried out to find the thermal diffusivity in photoacoustics where the variation in the amplitude of the PA signal for various chopping frequencies will be studied, for a fixed wavelength of the incident light.

Even though the PA signal was traced for different chopping frequencies, this is shown here for a particular chopping frequency in figure 2. Thermal diffusion length in any system is an unique property which means that the thermal energy from the surface can diffuse into a particular distance of the

Current Research Paper

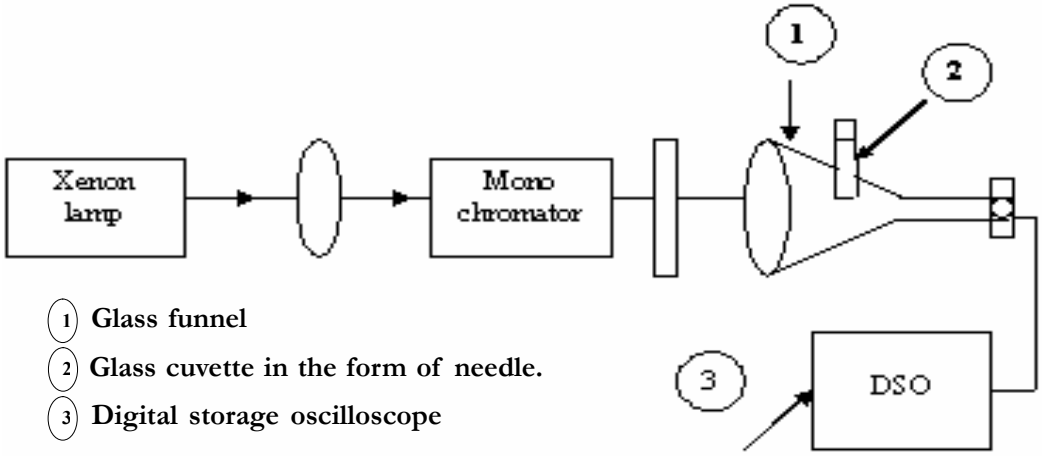

Figure 1: Photoacoustic spectrometer

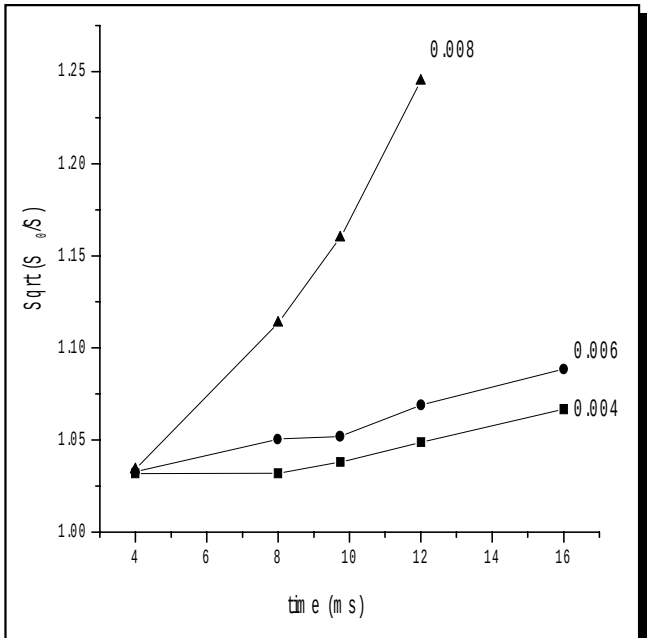

Figure 2: Photoacoustic signal amplitude with a function of time for different Cr(VI) concentrations (mole/lit).

sample and beyond which thermal energy cannot diffuse. Naturally this becomes a unique property and hence the thermal diffusivity. So,thermal diffusivity measurements were carried out for different Cr(VI) concentration using the present technique.

The intensity at the centre of the probe beam can be expressed by[11]

$$S = \frac{I_t - I_\infty}{I_t} = S_{t=0} = \frac{1}{\left(1 + 2n\frac{t}{t_c}\right)^2} \quad \text{where} \quad S_{t=0} = \frac{I_\infty - I_0}{I_0}$$

which is actually the variation of PA signal $\sqrt{\frac{S_0}{S}}$ where (S_0 - signal at time t = 0 and S - signal at time (t) as a function of time.From the slope of $\sqrt{\frac{S_0}{S}}$ as a function of time, the value of characteristic time constant (t_c) corresponding to each concentration is found out.To start with water and acetone are taken as the samples and measurements are done. The measured values of t_c for water and acetone are in good agreement with those reported in the literature[11]. Thermal diffusivity then calculated using these t_c values and the comparison with the literature is good.

The characteristic time constant t_c is related to the thermal diffusivity (D) and beam radius (ω) through the relation $t_c = \omega^2/4D$[11]. To eliminate the uncertainty in the determination of beam radius, a reference sample with known thermal diffusivity is used to determine the thermal diffusivity of the unknown sample. In our case, water was used as the reference sample. Thus,

$$D = \frac{D_{water} t_c^{water}}{t_c}$$

where D and t_c correspond to the Cr (VI) water. Using the present set up, the thermal diffusivities of water with different concentration of Chromium (VI) were determined and shown in TABLE 3.

Eventhough Lima et al.[8] have carried out open window PA technique, here we have obtained a calibration graph (Figure 4) for concentration of Cr(VI)

Current Research Paper

TABLE 3: Thermal diffusivity with Cr(VI) concentration

Molality	Thermal diffusivity x10^{-3} cm^2/s
0.01	0.056
0.008	0.066
0.007	0.074
0.006	0.1
0.005	0.15
0.004	0.2
0.003	0.29
0.002	0.33
0.001	0.49
0.000 (pure water)	1.43 (1.465)

and the change in thermal diffusivity.

Similarly a graph (Figure 3) is given connecting the concentration and the amplitude of the PA signal. The present measurements, figure 3 is compared with the work of Lima et al, where open window PA technique is used. The agreement is so good that the present technique is equally acceptable and the construction of the setup is very simple compared to Lima et al. As the concentration of chromium (VI) increases in water, the absorption also increases and so there is an increase in the strength of the PA signal.

But, figure 3 show an interesting behaviour here. As the concentration of Cr (VI) in water decreases, thermal diffusivity increases. This is possible because more and more ions will scatter more the incident energy in all direction in liquid and so there is a possibility in the reduction of thermal diffusion. For water this is 0.001465 cm^2/sec. i.e., when no Cr (VI) present. This clearly shows that very small concentration of Cr (VI) to the level of 0.05 μmol L^{-1} can be easily found out from the calibration graph figure 4. Thus it is demonstrated that the calibration graph connecting thermal diffusivity and concentration (Cr VI) is very useful than PA amplitude.

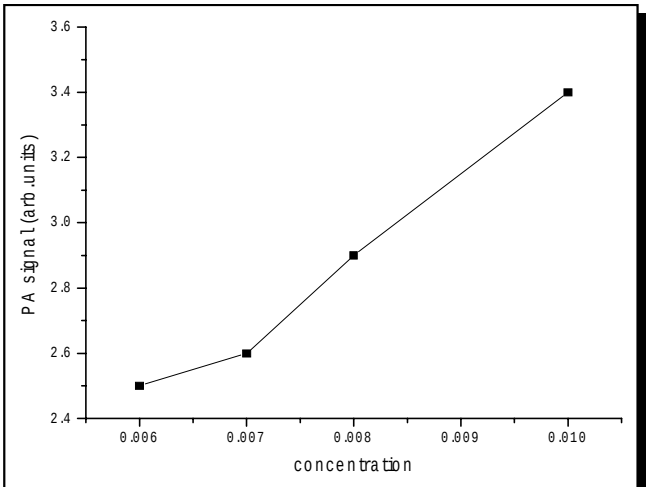

Figure 3: Cr (VI) concentration (mole/lit) with PA signal

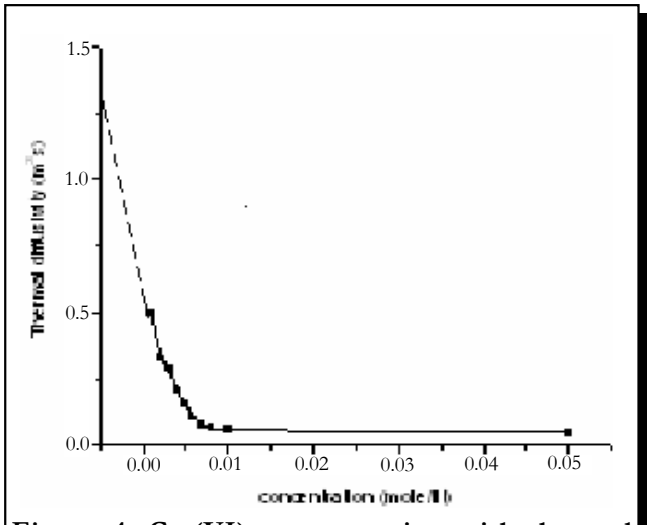

Figure 4: Cr (VI) concentration with thermal diffusivity Dotted line – extrapolation of the graph to zero concentration of Cr (VI) in water

Photoacoustic spectrum

Photoacoustic spectrum will be proportional to the absorption of the sample. The PA spectrum of the water sample was obtained by recording the PA signal as a function of the wavelength of the incident beam (from 400nm-700nm) for a constant modulation frequency of 20 Hz. The PA spectrum for liquid is normalized using the PA spectrum obtained for air in the allowed region of Xe lamp. This is given in figure 5 just for one sample. The uv-vis study on the same sample is 470nm.

We have obtained a peak at about 520 nm for Cr (VI) concentration of 0.05 mol L^{-1}. Andrzej et al.[12] has found the molar absorption coefficient at the absorption band maximum 546 nm.

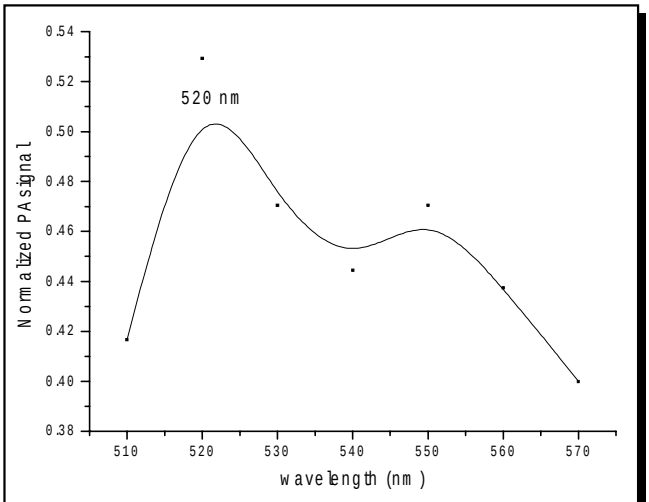

Figure 5: Photoacoustic spectrum (0.05mole/lit)

RESULTS AND DISCUSSION

Everyone is aware that Cr (VI) in water is dangerous to human being and so intensive research activities are going on in this field. The water near tanning industries are prone to such contamination and the concentration there would be above the border line of 0.9 $\mu molL^{-1}$. Sophisticated experiments like sequential injection analysis and multivariate curve resolution[13], apart from ion chromatography, uv vis, catalytic method and so on are available for this study. Here a simple photoacoustic technique has been used to find the Cr(VI) concentration which can be made portable. The present measurements on thermal diffusivity with Cr(VI) concentration is very useful than PA amplitude versus concentration. Now using the figure 5 any concentration of Cr (VI) in water down to a level of $\mu molL^{-1}$ can be found out.

CONCLUSIONS

A simple photoacoustic technique is proved to be very successful to find out the Cr(VI) concentration in water as other methods are not only complex in measurements but also the amount of sample needed would be much more compared to the present PA technique.

ACKNOWLEDGEMENTS

One of the authors (G.Krishna Bama) acknowledges University Grants Commission, New Delhi for providing a fellowship under FIP scheme to carry out this work in the School of Physics, Madurai Kamaraj University, Madurai.

REFERENCES

[1] http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/chromium 6/Cr^{+6}index.htm.
[2] International agency for research on cancer, WHO, Chromium, Nickel and welding, IARC Monographs on the evaluation of Carcinogenic Risks to Humans, IARRC, Lyon, 49 **(1990)**.
[3] National Toxicology Program, Chromium Hexavalent Compounds, Ninth Report on carcinogens, NTP, Department of Health and Human Services, **(2000)**.
[4] Water Quality criteria (Ecological Research Series) (Washington, DC: EPA), **(1972)**.
[5] B.S.Scidel, W.Faubel; Opt.Eng., **36**, 469 **(1997)**.
[6] R.Michalski; Acta Chromotographica, 15 **(2005)**.
[7] Angelina Militcheva Stoyanova; Turk J Chem., **29**, 367 **(2005)**.
[8] J.A.P.Lima, E.Marin, S.L.Carodoso, O.Delgado-Vasallo, M.G.daSilva, M.S.Sthel, C.E.N.Gatts, A. Mariano, C.E.Rezende, A.R.C.Ovalle, M.S.Suzuki, H.Vargas; Analytical Sciences, **17**, 530 **(2001)**.
[9] B.Hartmann; J.Acoust.Soc.Am., **65**, 1392 **(1979)**.
[10] M.Wawrzenczyk, M.Cyfert; Pol.J.Chem., **68**, 1615 **(1994)**.
[11] C.V.Bindhu; Ph.D thesis, Cochin University of Science and Technology, June **(1998)**.
[12] Andrzej Bobrowski, Jan Mocak, Janusz Dominik, Helena Pereira, Boguslaw Bas and Wieslaw Knap, Acta Chim.Slov., **51**, 77 **(2004)**.
[13] V.Gomez, A.Pasamontes; M.P Callao http:// www.quimica.urv.es/quimio.