

METHOD BASED ON A COLLOID INDICATOR, USED TO IDENTIFY METALS FROM DRINKING WATER

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The paper presents a new analytical method for identifying of chromium, copper and lead from drinking water [1,2]. Its novelty consists in introducing a selected methyl orange –dye for identification and dozing of three metals. The method is applicable both for drinking and mineral water in which the degree of interaction with other compounds or impurities is relatively low. The three metals are usually qualitatively and quantitatively analysed by standard classical methods: colorimetry or atomic absorption spectrophotometry. But these methods require some reagents, also are energy consuming and have high cost. The new method is cheaper, faster and the colloidal dye can be applied *in situ*. The method for determination of: chromium, copper and lead from drinkable waters consists in introducing a fixed amount of dye and measuring absorption of the formed *metal-dye associates*. Most organic dyes are basic or acids compounds and present colloidal association [3,4]. Their tendency to associate in colloidal micelles was first studied by conductivity. Due to the flat shape their molecules form layered lamellar micelles, resembling like a “package of cards” [5,6]. Methyl orange is recognized as a colloidal type dye. The intensity of characteristic bands is proportional to the amount of colloid indicator (methyl orange- dye) and number of *metal-dye associates* present in the system. Thus the concentration of metals in water can be determined. Due its capacity to determine qualitatively and quantitatively the three selected metals in drinking water, the paper presents ecological importance.

Keywords: new analytical method, colloid indicator (methyl orange- dye), drinking water, metals identification and dozing, metal-dye associates

INTRODUCTION

The paper consists in selecting and introducing a dye: methyl orange– $C_{14}H_{14}N_3NaO_3S$ (4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt) to identify and dose three metals from drinking water: chromium, copper and lead.

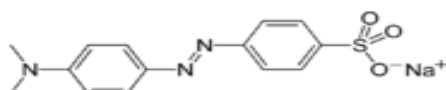


Figure 1: Methyl orange [3]

Removing of metal ions from drinking water can be done by ion exchanger or electrodialysis. The paper presents a new efficient and fast spectral method to determine: chromium, copper and lead in drinking water, based on introducing a fixed amount of methyl orange in their aqueous solutions having different concentrations and measuring absorption of metal-dye associates.

MATERIALS AND METHODS

Chromium, copper and lead 1% solutions were prepared separately in distilled water. The sample was introduced into a GBC spectrophotometer model 918, equipped with 1 cm thick quartz cuvettes. The absorbance value was read at $\lambda = 300$ nm and recorded. The calibration curve of methyl orange in water was determined. A fixed amount of 0,01% colloidal dye- methyl orange was added to the analyzed sample. The UV-VIS spectrum was recorded. Readings and recording of absorbance values were done at the same wavelength. The calibration curves of the three metals in water were plotted. In comparison, for the three metals studied by atomic absorption spectrophotometry, these are determined by turning to vapours, with the property of absorbing radiation proportional to the concentration and visualization in the form of impulses. Metal concentration is calculated depending on the number of impulses according to a calibration scale. In conclusion, methyl orange was selected as indicator for the elaborated method.

EXPERIMENTAL

The studied metals are determined classically, by colorimetry or atomic absorption spectrophotometry. The calibration curves of the three metals obtained by atomic absorption spectrophotometry are presented in Figures 2-4.

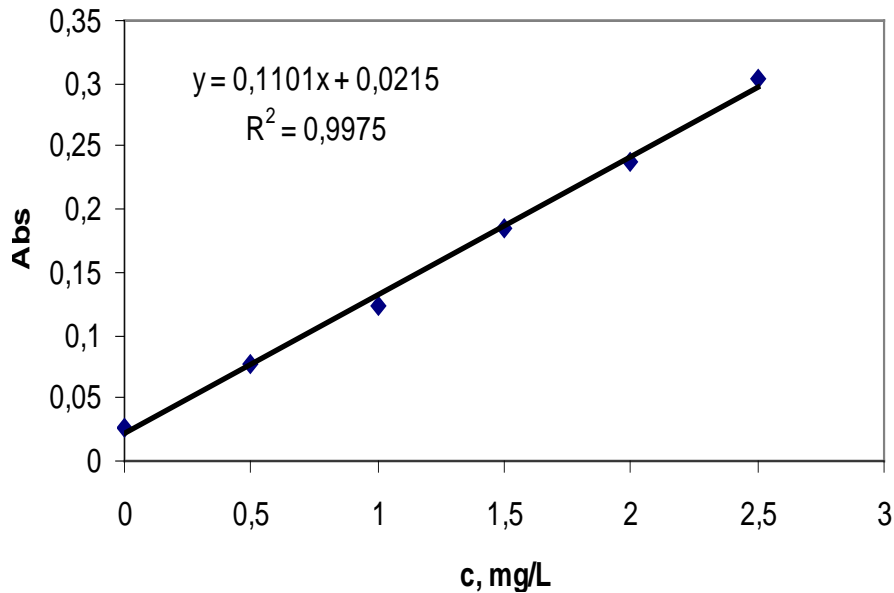


Figure 2: Calibration curve of **chromium** in water, obtained by atomic absorption spectrophotometry

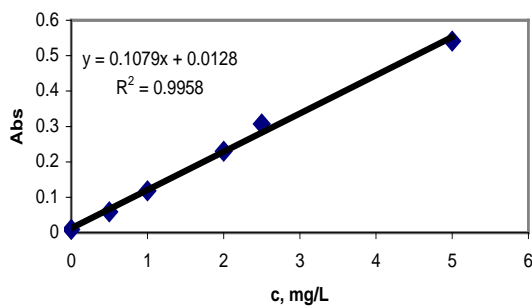


Figure 3: Calibration curve of **copper** in water, obtained by atomic absorption spectrophotometry

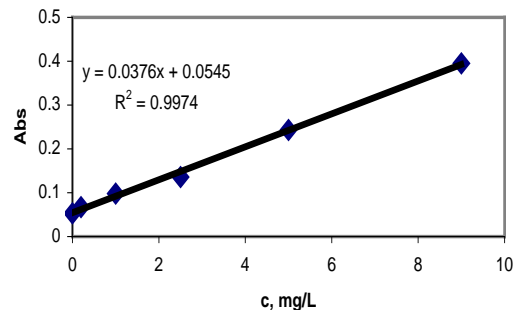


Figure 4: Calibration curve of **lead** in water, obtained by atomic absorption spectrophotometry

Atomic absorption spectrophotometry being a high cost and time consuming method. Faster methods are required and the method based on the colloidal dye methyl orange is proposed. The colour intensity of the dye solution in water changes visibly with dye concentration: for very diluted methyl orange solutions the colour is yellow, and by increasing concentration it turns into orange. The methyl orange dye behaves like a surface active compound: the concentration corresponding to colour change is called critical concentration and indicate a different aggregation way of dye molecules in water. Methyl orange a colloidal dye, [1-6] presents at high concentrations the association

phenomenon, leading to the occurrence of a supracolloidal solutions. Although most organic dyes are basic or acid compounds, and thus in colloid state are association polyelectrolytes, they cannot be included among the anionic or cationic agents, due to their different chemical structure, having a totally different association mechanism compared with the classic surface active compound. Their tendency to associate forming colloidal micelles was emphasized for the first time by C. Robinson in 1935 [7], by conductivity, as for the other association polyelectrolytes. Due to their flat shape (which aromatic cycles have, from which colloidal dyes are usually made up of), their molecules associate by the overlapping of these cycles, forming lamellar micelles layered in the shape of a “pack of cards”, called after the name of the scientist who discovered them **Scheibe aggregates** (G.Scheibe, 1935 [8]). As a result of this association mechanism, the ratio between the section of associated particles and the number of remainings is almost unchanged, just like conductivity. Neither diffusion nor the solubilizing capacity or the capillary activity of colloidal dyes present the systematic anomalies found in classic surface active compounds. In the critical concentration domain of colloidal dyes very interesting optical effects and characteristics manifest, such as a change in the absorption or fluorescence spectrum. The dye was studied as indicator for the three metals. The “fingerprint” spectrum of a known concentration of **chromium** in water (Fig.5) was recorded and then that of the chromium solution containing a fixed quantity of methyl orange (fig.6).

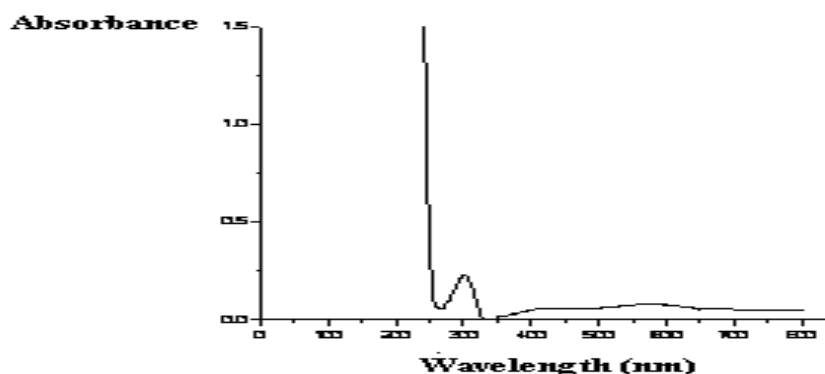


Figure 5: UV-VIS spectrum (“fingerprint”) of **chromium** in water, $c = 1\%$

The spectrum presented in Fig.5, shows that chromium in water ($c = 1\%$) has 2 absorption maxima, at 233.45 nm and 300,99 nm. Upon adding a constant amount of 0.01% methyl orange (MO), an absorption peak occurs in the UV-VIS spectrum at 526.10 nm (Fig.6).

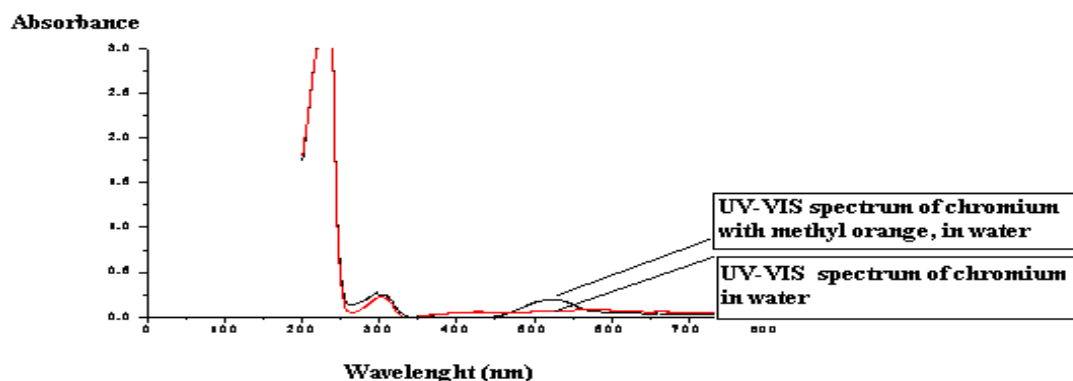


Figure 6: UV-VIS spectrum of **chromium** ($C_{Cr} = 1\%$) and **chromium with methyl orange** in water ($C_{Cr} = 1\%$, $C_{MO} = 0.01\%$)

The spectrum presented in Fig.7 indicates a concentration of **copper** in water of 0.863% and has an absorption maximum at 299,29 nm. On adding a constant concentration of 0,01% MO, an absorption peak occurs in the UV-VIS spectrum at 526,10 nm, specific to the colour.

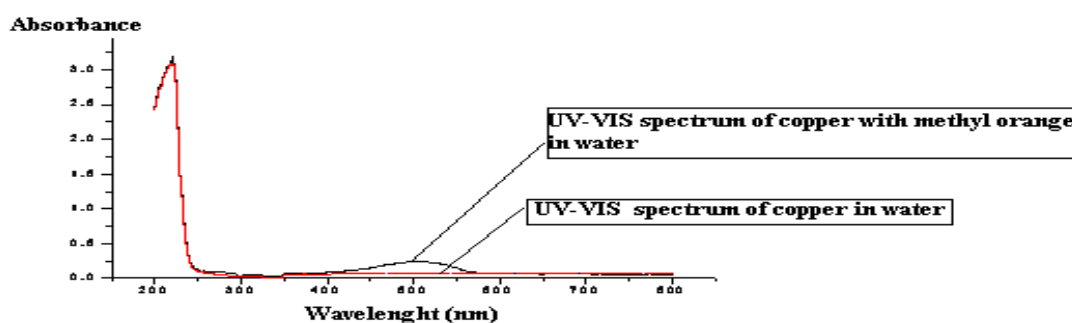


Figure 7: UV-VIS spectrum of **copper** in water ($c = 0.863\%$) and of **copper with methyl orange** in water ($C_{Cu} = 0.863\%$, $C_{MO} = 0.01\%$)

A constant concentration of methyl orange of 1,45% was added to the **lead** solution, and the obtained UV-VIS spectrum is presented in Figure 8. Absorption maxima are recorded at 305,30 and 526,10 nm (corresponding to the colour).

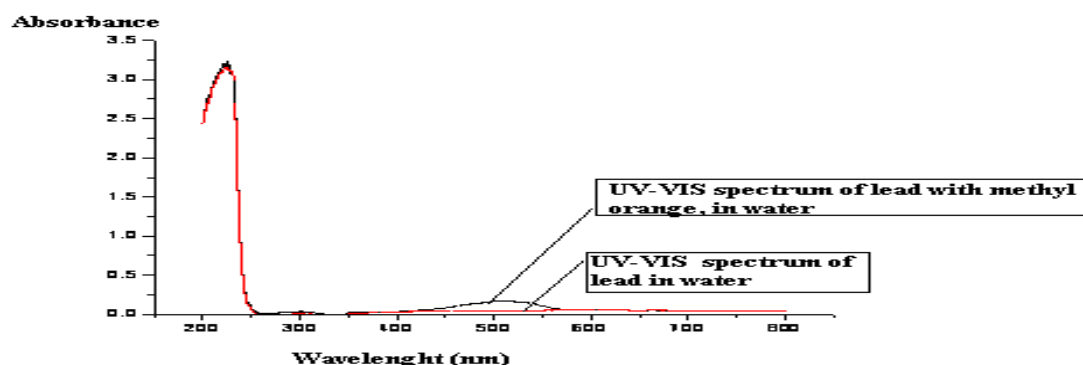


Figure 8: UV-VIS spectrum of **lead** in water ($c = 1.45\%$) and **lead with methyl orange**, in water ($C_{Pb} = 1.45\%$, $C_{MO} = 0.01\%$)

It was noticed that the indicator for studied metals in water is methyl orange (MO), as it indicates the absorption peaks of metal and the quantitative value (absorbance is proportional to the quantity of metal introduced), but also has a characteristic peak at wavelength 526,10 nm (table 1). Experimental data are presented in Table 1:

Table 1: Experimental results for methyl orange indicator of the 3 metals in water

No	Metal conc. in water	MO conc.	Metal absorbance	Metal absorbance with MO
1	1% Chromium	0,01%	at $\lambda=300,99$ nm; Abs= 0,2454	at $\lambda=300,99$ nm; Abs=0,2477
2	1% Copper	0,01%	at $\lambda=299,29$ nm; Abs=0,0103	at $\lambda=299,29$ nm; Abs=0,0107
3	1% Lead	0,01%	at $\lambda=305,30$ nm; Abs= 0,0066	at $\lambda=305,30$ nm; Abs= 0,0062

The calibration curves of the dye and the metals with methyl orange in water were determined. UV-VIS spectra of methyl orange in water for different concentrations and the calibration curve are presented in Fig. 9 and 10.

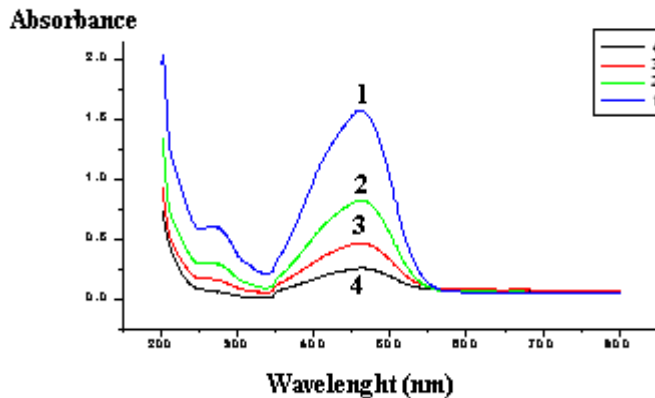


Figure 9: UV-VIS spectra of methyl orange in water for different concentrations: **1 = 1.0%**; **2 = 0.5%**; **3 = 0.25%**; **4 = 0.125%**

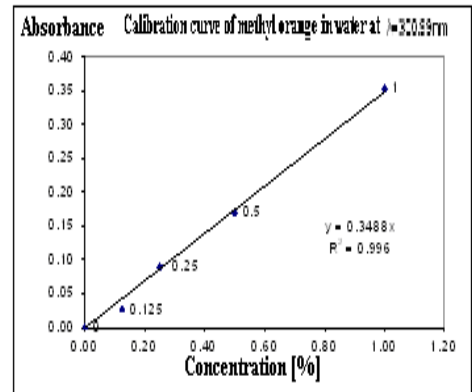


Figure 10: Calibration curve for methyl orange in water

The calibration curve of chromium in water is given in Figure 11.

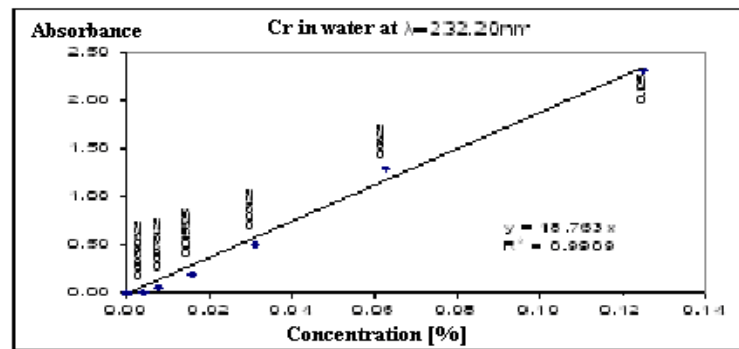


Figure 11: Calibration curve for chromium in water

The UV-VIS spectra of chromium with methyl orange in water ($c = 0,01\%$ = constant) for different chromium ions concentrations and the calibration curve of chromium with methyl orange are illustrated in Fig. 12-14:

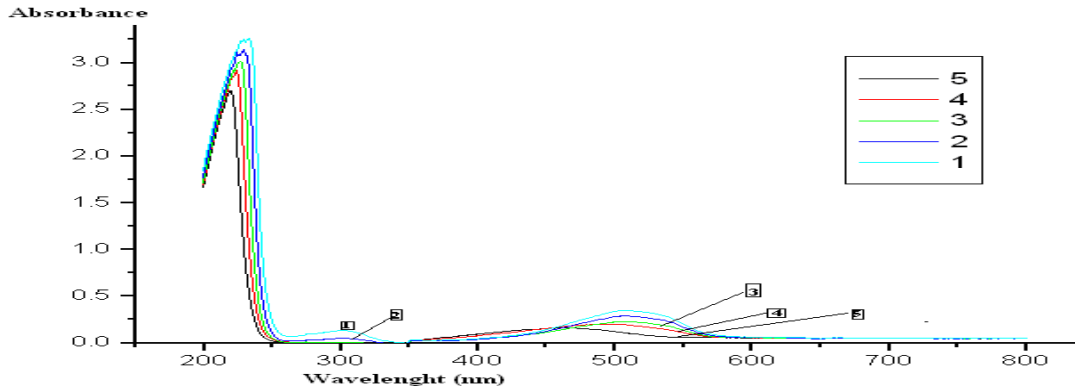


Figure 12: UV-VIS spectra of chromium with methyl orange ($c_{MO}=0.01\%$ =constant) in water for: **1**=0,5%; **2**=0,25%; **3**=0,125%; **4**=0,0625%; **5**=0,0312%

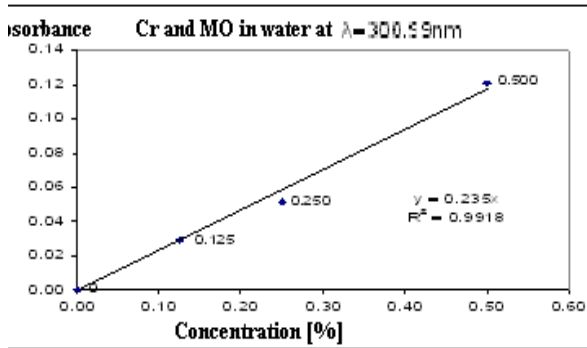


Figure 13: Calibration curve of chromium with methyl orange ($c_{MO} = 0.01\%$ = constant), in water

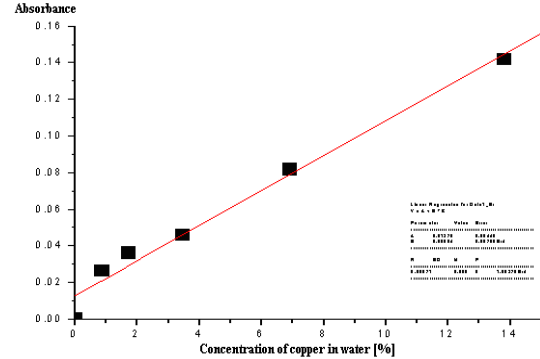


Figure 14: Calibration curve of copper in water

The UV-VIS spectra of copper with methyl orange in water ($c = 0.01\%$ = constant) for different copper concentrations and the calibration curve of copper with methyl orange are illustrated in Fig. 15-16:

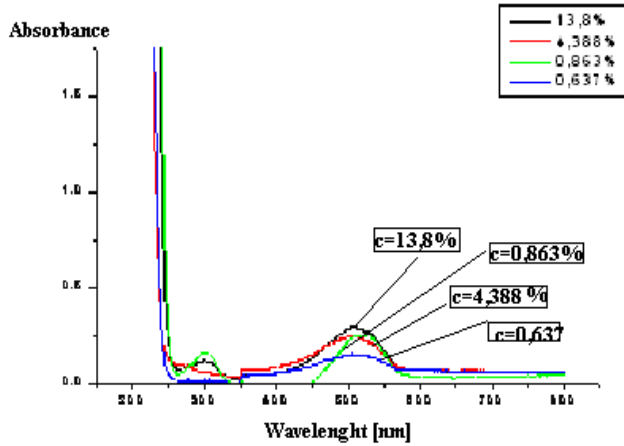


Figure 15: UV-VIS spectra of copper with methyl orange ($c_{MO} = 0.01\%$ = constant) in water, for different concentrations

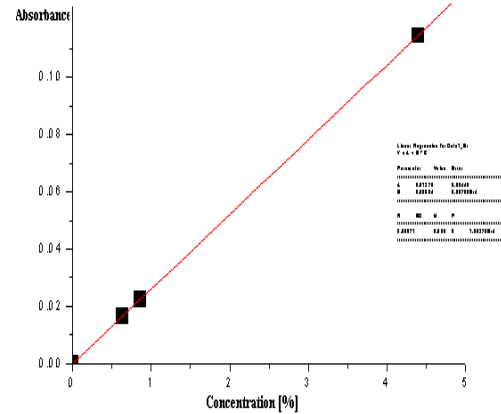


Figure 16: Calibration curve of copper with methyl orange ($c_{MO} = 0.01\%$ = constant), in water, for $\lambda = 299.29 \text{ nm}$ = constant

The Calibration curve of lead in water for different concentrations is presented in Fig.17:

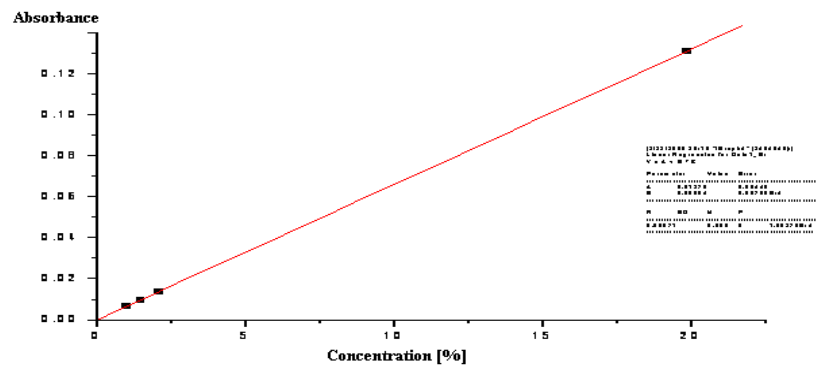


Figure 17: Calibration curve of lead in water

The UV-VIS spectra of lead with methyl orange in water ($c = 0.01\%$ = constant) for different lead concentrations and the calibration curve of lead with methyl orange are illustrated in Fig. 18 and 19:

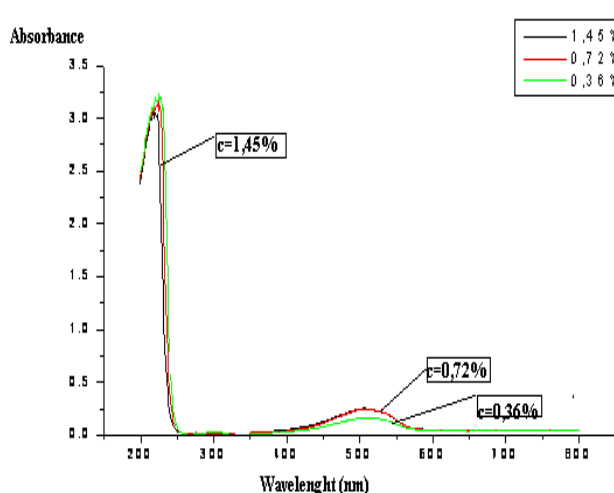


Figure 18: UV-VIS spectra of lead with methyl orange ($C_{MO} = 0.01\%$ = constant) in water, for different concentrations

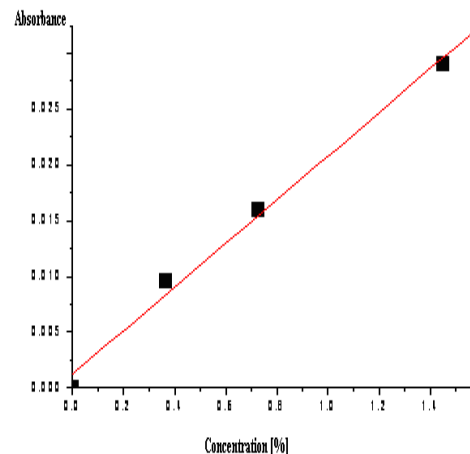


Figure 19: Calibration curve of lead with methyl orange ($C_{MO} = 0.01\%$ = constant), in water, for $\lambda = 305.30\text{nm}$ = constant

CONCLUSIONS

The technical issue which this paper solves consists in obtaining of metal content from drinking water by means of a new analytical method using a colloidal indicator- methyl orange. The intensity of characteristic bands is proportional to the "colloidized" indicator amount (methyl orange- dye) and the number of associates in the system (metal dye) and thus metal concentration in aqueous solutions can be determined.

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