

Determination of Chromium(VI) and Copper(II) in Organic Solvent — Solution by Liquid Core Optical Fiber Spectrophotometry

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Abstract : A new hollow fiber filled with the lower refractive index liquid as core constructs a liquid core optical fiber(LCOF). The LCOF have been used as colorimetric cell to determine elements Cr and Cu in the presence of 70%— 50% ethanol or 50% dioxane aqueous solution, based on colored complex of Chromium(VI) with Diphenylcarbazid(DPC) and copper with Chromaurd S (CAS) respectively. The sensitivity (1/ng/ml) of calibration curve of Cr and Cu are 0.052, 0.017 over the range 0 — 25, 0 — 24(ng/ml)respectively. The Cr in the animal gum and Nation Standard of China are determined with recoveries of 94 — 102%

Keywords : Liquid core optical fiber, aqueous solution, Cr, Cu.

1. Introduction

Spectrophotometric method is one of the most important ways in Chemical analysis. In order to improve the sensitivity, a long capillary tube was used to serve

as a Colorimetric cell instead of the conventional one[1,2]for determination of I, P Cu etc . The sensitivity increases by a factor of 100 — 1000 times when capillary tube is 1-4m long . We have also measured Au, Ag, Te, etc by using of 1m long LCOF and the sensitivity is about

50 — 100 times as many as that of 1cm cell[3,4]. However, tube is made of quartz or glass and LCOF can not guide light until the refractive index of liquid is greater than 1.46. Therefore, only extraction method from high refractive index solvents such as carbon tetrachloride or benzene are suitable, which brings a lot of troubles as well as toxic hurt to analysts. For the purpose of developing color directly from water phase a new kind of hollow fiber (i.d. 800 μm , o.d. 1.6mm; refractive index 1.34 at $\lambda = 5.4\text{nm}$) was found that the fluid with refractive index as low as 1.346 can act as cores. 70% alcohol or 50% 1,4 dioxane aqueous water solution have been successfully prepared to serve as cores by setting aside mixture 16 hours so as to avoid bubbles. Based on this, the LCOF Spectrophotometry are developed to determine chromium(VI) and copper(II) with diphenylcarbazide and chromaurd S in the mixture solution of organic solvents and water respectively.

2. Experimental

2.1 Apparatus

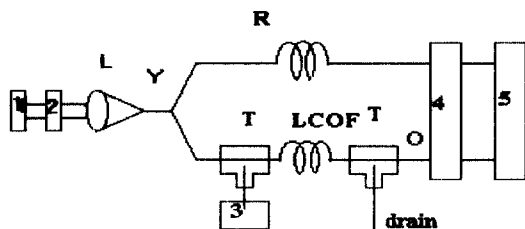


Fig 1. Setup of LCOF spectrophotometry

1. light source; 2. monochromator; 3. pump; 4. detector: PIN silicon photodiode, DC Amplifier, A/D converter, microcomputer; 5. display; L. convex lens; Y. Y — type optical fiber; T. T connector; O. optical fiber; R. reference optical fiber.

A halogen tungsten lamp (24V, 250W) is used as light source. The monochromatic light through monochromator is divided into two beams by Y — optical fiber located after a convex lens. one beam is guided to liquid core optical fiber to determine the concentration of element, the other one pass through solid optical fiber as reference to adjust the unstability of light source. Then the two beams are received by PIN silicon photodiode respectively, amplified and converted by A/D, finally, become digital signals. The light intensity, absorbance, concentration of element and correlative Coefficient of the calibration curve are displayed by the computer. T connector can standwith pressure to prevent fluid from flowing out. Besides, it is a coupler through which the optical fiber (i.d. 600 μm) is inserted into hollow fiber (i.d. 800 μm) to guide light from light source to LCOF and LCOF is constructed when fluid is introduced into hollow fiber through the space of optical fiber and wall of hollow fiber by pump.

2.2 Operation

LCOF is 1.1m in length, looped diameter 15cm. Introduce the Sample solution into LCOF by a peristaltic pump at the speed of flow of 2-3 ml/min for 1-2 min, switch on the pump until the light intensity keep stable, then measure absorbance at selective wavelength against the reagent blank.

2.3 Reagents and solution

Sulphuric acid, nitric acid, hydrochloric acid, ethanol used are of G.R. reagents, the other reagents are of analytical grade. Water used is demineralized. After prepared, water solution of 70% ethanol or 50% 1,4 dioxane(V/V) are set aside for a overnight under condition of 22 $^{\circ}\text{C}$ below in order that bubbles leave slowly from the mixture.

Standard Cr(VI) solution: 0.1mg/ml of potassium dichromate(GR) stock solution is diluted to 1(μ g/ml) on the day of use.

Standard Cu(II) solution: 0.1 mg/ml of copper stock solution prepared from 99.99% copper is diluted to 1(μ g/ml) on the day of use.

2.4 Analytical procedure of chromium(VI)[5] and copper(II)[6].

putting 0.00, 0.05, 0.10, 0.15, 0.20, 0.25ml of standard 1(μ g/ml) Cr(VI) solution into 25ml standard flask with pipette, then, adding 0.60, 0.55, 0.50, 0.45, 0.40, 0.35 ml of water, adjusting the acidity to 0.2N with sulphuric acid and putting 0.2ml of 0.05% DPC solution, finally diluting to the mark with 70% ethanol or 50% 1,4 dioxane aqueous solution and mixing thoroughly. After 30 min, measuring the absorbance at 540 nm against a reagent blank with the LCOF spectrophotometric system illustrated in Fig. 1

The analytical procedure of copper(II) is mainly in accordance with one of the chromium, but adjust the acidity to PH=6.0, add both 0.2 ml of buffer solution

(PH=6.4) and 0.05% CAS solution, after 30 min, measure the absorbance at 590nm against the reagent blank.

2.5 Determination of Cr(VI) in samples.

weigh the animal gum 0.5000g in the quartz crucible, add 1 – 2 drops of concentration nitric acid, heat the sample until in ashes, then, in the muffle furnace at 550 °C, ignite 1-2 hr, cool and dissolve in nitric acid (to avoid co-precipitation because of its high calcium containing). Next, transfer it into 10 ml standard flask, dilute to the mark with water, pipette appropriate amounts of this solution into a 100ml beaker, put drops of 1% potassium permanganate solution, then, boil the mixture solution for 5 min and cool is followed. After that, add a little urea and mix. At last, add 1% sodium nitrite solution and dropwise with frequent shaking. As soon as the purplish colour is discharged, transfer the solution to 25 ml standard flask to determine Chromium(VI) as above procedure.

The results of determination of Cr, Cu are shown in table I, II and III.

Table I . Standard curve and sensitivity

element	reagent concentration (v/v)	linear regression equation (C:ng/ml)	linear range(ng/ml)	correlative coefficient	detection limit (3 σ) (ng/ml)	n
Cr	70% ethanol	A=0.052C+0.019	0 – 25	99.9	0.14	9
	50% dioxane	A=0.047C - 0.013	0 – 25	99.9	0.15	10
Cu	70% ethanol	A=0.017C - 0.008	0 – 24	99.2	0.16	8

σ : The standard deviation of reagent blank

n : The repetition times of determining reagent blank

Table II Chromium determination of samples

sample	standard value (μ g/ml)	AAS (μ g/ml)	LCOF	n	RSD (%)
GSBE50009 – 88	2.50 ± 0.075		2.22 ± 0.139 (μ g/ml)	5	6.3
animal gum		23.98	23.16 ± 0.56 (μ g/g)	5	2.4

AAS : The measured by atom absorption spectrophotometry

LCOF: The measured by LCOF spectrophotometry

Table III. Recovery of chromium

sample	Cr in sample (ng/ml)	added (ng/ml)	found (ng/ml)	n	recovery (%)
animal gum	11.289	10	21.052	4	99
synthetic water	5.00	4	8.50	3	94
Cu 1, Cd 1, Zn 2, Cr 5(ng/ml)	5.00	8	12.5	3	96
	5.00	16	21.5	3	102

The calibration curve was found to obey Beer's Law over the range 0 — 25(ng/ml) for Cr and 0 — 24(ng/ml) for Cu respectively. In the presence of 70% ethanol or 50 % dioxane aqueous solution for determination of 5(ng/ml) Cr, the relative standard deviations are 6.9 % and 1.0 % respectively for eight repetitions; in the presence of 70 % ethanol water — solution for 10 (ng/ml) Cu the RSD is 2.2% based on ten repetitions.

3. Results and Discussion

The results demonstrate that the LCOF spectrophotometry enhance the sensitivity to the level of a few nanogram per milliliter without preconcentration. Uniform and bubble — free 70% ethanol or 50% dioxane aqueous solution are qualified as the solvents in LCOF spectrophotometry, which have the advantage of simplifying the analytical procedure. Moreover, we can find that some conventional methods can be applied to LCOF system, but sensitivity reaches ng/ml . At present,

relative research are being undertaken on analytical ways and instrument of LCOF.

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References

1. Keiichiro Fuwa, Wei Lei, Kito Fujiwara, *Anal. Chem.*, 55, 951, (1983).
2. Wei Lei, Kita Fujiwara and Keiichiro Fuwa, *Anal. Chem.*, 56, 1640, (1984).
3. Yuanmin Liao, Minzhao Fen, Qushe He, *Anal. Chem.*, (China), 21, 70, (1993).
4. Qushe He, Wang Wei, Wang tao, *Spectroscopy and Spectral Analysis*, (China), 13, 123, (1993).
5. Shuijie Hong, *Environmental Pollution Analysis*, Vol. 1, Inorganic Analysis, second edition, Science Press(China), 1987.
6. 西田宏, 西田妙子, *Bunseki kagaku*, 25, 55, (1976).