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Spectrophotometric Determination of Chromium, Copper, Nickel and Iron in Electroplating Hydroxide Sludges

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The aim of the present work was to search a convenient, simple and inexpensive method to determine the metals in electroplating hydroxide sludges. The analytical methods are characterized by sensitivity, selectivity and accuracy but for economic reasons and of course the availability of equipments and products, the UV-visible spectrophotometry was used. We have undertaken the study of the influence of different cations present in the same solution on the determination of metal. After conducting several tests on solutions prepared in the laboratory and then on the solutions used to dissolve different samples of industrial waste, the result revealed that it is possible to use spectrophotometric method to assess the amount of metals in electroplating sludges, provided that we followed a well-defined scheme so as to avoid all the possible interference.

Keywords: Industrial, Waste, Electroplating, Sludges, UV-visible spectrophotometry.

INTRODUCTION

Process wastewaters from metal finishing industry contain cyanides and heavy metals like copper and nickel in appreciable concentrations [1-3]. Neutralization and precipitation treatments of these wastewaters destroy cyanides and remove heavy metals as hydroxide sludge [4]. Disposal of these hazardous wastes results in environmental pollution and loss of metals. The separation of a mixture of metal hydroxides in sludge requires an analytical method to determine the amount of each hydroxide and also to monitor stages of separation. This method should be sensitive, selective, precise and cost effective. Today, there are three most adopted methods *e.g.*, UV-visible spectrophotometry, atomic absorption spectroscopy and X-ray fluorescence [5-12] which are characterized by sensitivity, selectivity and accuracy but for economic reasons and of course the availability of equipments and products we prefer using UV-visible spectrophotometry owing to its availability in most laboratories and easiness to implementation without special training. In addition it meets the basic requirements of the automated analysis methods such as reaction time, small samples, high sensitivity and selectivity. According to the definition recommended by the Department of Analytical Chemistry of the International Union of Pure and Applied Chemistry (IUPAC), the reagent which reacts with a limited number of elements is considered as selective whereas a reagent is considered as specific when it reacts with only one element in certain circumstances [12]. In the same way the selectivity and specificity are defined in the coloured reactions and analytical methods. The selectivity depends upon the nature of the reagent used, the degree of oxidation of the element, the pH of the medium and the nature of the agent used to complex the interfering elements. Nevertheless, despite of the use of all these factors, some elements still interfere during the assay. Therefore, we need to separate the measured element or *vice versa*. There are a number of separation techniques including precipitation and co-precipitation, organic solvent extraction and ion exchange, *etc.* [5]. There are few specific reagents for a specific element. A rare example is the cuproine reagent for copper(I) and patophenanthroline reagent for iron(II). As the change of the oxidation state of certain elements leads to a lack of reaction with some of reagents, for example, in the determination of niobium by thiocyanate, the iron ion does not interfere if it is reduced to iron(II). The selectivity of several methods depends on the choice of pH of the medium suitable for reaction, that is, the pH values affect the equilibrium of the reaction which leading to a right or left shifting and therefore a change in the colour of the solution. The creation of selectivity in spectrophotometric methods generally resulted by masking interlaced ions, which is

obtained by changing the interfering element to a stable complex using reagent provided that this does not affect the colour of the reaction under study. Thus we get high selectivity by using the appropriate masking agents and pH value [5-12].

EXPERIMENTAL

Determination of iron: There are several methods for the spectrophotometric determination of iron(II) and iron(III), such as the 1,10-phenenthroline and 2,2'-dipyridyl, thiocyanate method, bathophenanthroline method and the sulphosalicylate method [12,13]. These methods differ by either sensitivity or selectivity. The last method is regarded as less sensitive than the other ones and the method of thiocyanate is the earliest sensitive commonly used method but the colour of complex of the iron(III) with thiocyanate is unstable due to the reduction of iron(III) by-SCN^-. In fact the colour slightly decreases after 0.5 h and almost 50 % after 6 h. Among these methods the most commonly used are those of the 1,10-phenenthroline and 2,2'-dipyridyl and thiocyanate. The method of phenanthroline and 2,2'-dipyridyl have the same sensitivity. These two reagents give a brown colour with iron(II) ions. It is necessary to choose the method which gives stable complexes, a stable colour and a high sensitivity. The reagents 1,10-phenanthroline and 2,2'-bipyridyl form coloured complexes with other elements such as (Cu, Os, Re, Bi, Ni, Co, Ag). The complex of copper(I) with 1,10-phenanthroline was separated from iron(II) by extraction by *n*-octanol. Bivalent cations such as zinc and cadmium ions, form with 1,10-phenanthroline uncoloured complexes more stable than iron(II) complexes and can be masked by the EDTA. The copper(II) ions are masked by thioglycolic acid. Phosphate, oxalate and fluorine do not interfere if the pH of the medium is less than 4. The method of 1,10-phenenthroline is used for the determination of traces of iron in the alloys, metals, minerals, water, foodstuffs and in various industries [6,7,12-17].

Method of 1,10-phenenthroline: Iron(II) and total iron can be determined by reduction of iron(II) with a reducing agent such as hydroxylamine hydrochloride in acidic medium buffered with acetic acid and ammonium acetate (CH_3COOH/CH_3COONH_4). Under these conditions the 1,10-phenenthroline gives a stable brown complex with iron. This method has a very high sensitivity at λ_{max} = 512 nm with the molar absorptivity $\varepsilon = 1.1 \times 10^4$ mol $^{-1}$ cm $^{-1}$, specific absorptivity a = 0.2 mL g^{-1} cm^{-1} and the detection limit of this method is 3 mg/L.

Effect of different cations on the determination of iron: After the Determination of λ_{max} (510 nm) and the calibration curve (0.04-2 mg/L of Fe^{II}) we have studied the effect of the cations Cr, Ni, Cu. A series of solutions of fixed iron concentration is prepared and different proportions of the studied cations are added. The absorbance is measured at λ_{max} = 512 nm (Fig. 1).

Determination of copper: Copper like other metals gives several coloured complexes with different reagents and therefore several colourimetric methods. The appropriate reagents are dithizone, dithiocarbamate, cuprizone and oxalyldihydrazide acetaldehyde. The most sensitive methods are dithizone method and that using oxalyldihydrazide acetaldehyde [7,18-24].

Method of oxalyldihydrazide acetaldehyde: At pH = 9.3, copper forms with copper oxalyldihydrazide acetaldehyde a purple complex which enables to perform a colourimetric determination with a detection limit of 6 mg/L.

Effect of different cations on the determination of copper: After determination of λ_{max} (540 nm) and the calibration curve (0.2-1 mg/L of Cu^{II}) we have performed the study of the influence of Cr, Fe and Ni. A series of solutions of a fixed concentration of copper is prepared and different percentages of the studied cations are added. The absorbance is then measured at λ_{max} = 540 nm (Fig. 2).

Determination of nickel: Many organic reagents give fixed and coloured complexes with nickel ions and the most important of these reagents are dioxime. The Method using this reagent is selective and sensitive. Among the sensitive reagents are: 1-(2-pyridylazo)-2-naphthol (PAN) and pyridine-2-quinolyl-2-aldehyde hydrazone (PAQH).

The method using dioxime is selective for nickel and involves two reagents *i.e.*, dimethylglyoxime (DMG) and α-frill dimethylglyoxime (DMG).

The ions of (Au, CrO_4^{2-}) affect the determination of nickel. Iron(II), cobalt(II) and copper(II) form with the DMG stable coloured complexes. To avoid the influence of these ions, EDTA is used as masking agent. DMG is the method used for the determination of nickel in various alloys, rocks, petroleum, water, soil and air [6,7,12,13,25-30].

Method of dimethylglyoxime (DMG): The dimethylglyoxime forms with nickel, in the presence of an oxidant such as potassium persulphate $K_2S_2O_8$ and in a neutral or ammoniacal medium, a very stable red-brown complex. In alkaline

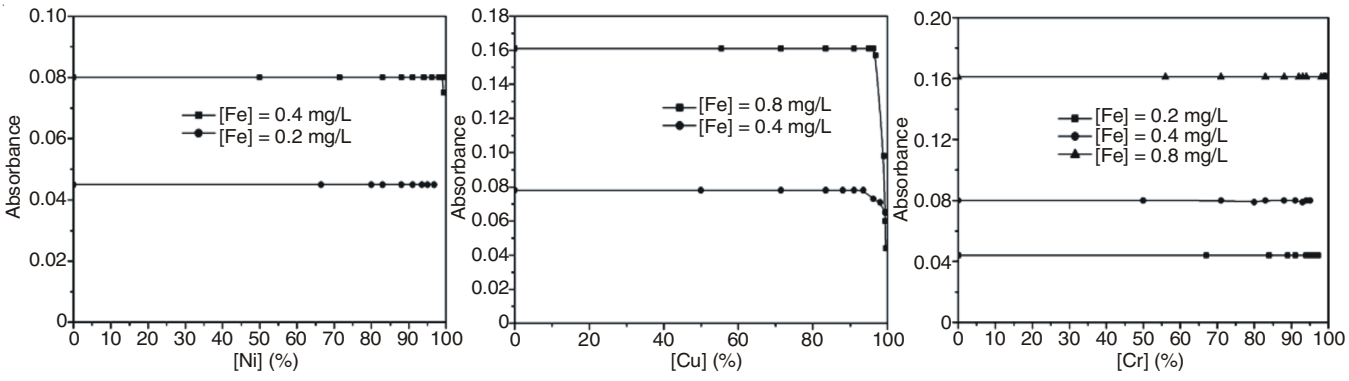

Fig. 1. Effect of metal ions on the absorption of solutions with different concentrations of the complex iron(II) 1,10-phenenthroline: (A) nickel effect, (B) copper effect, (C) chromium effect

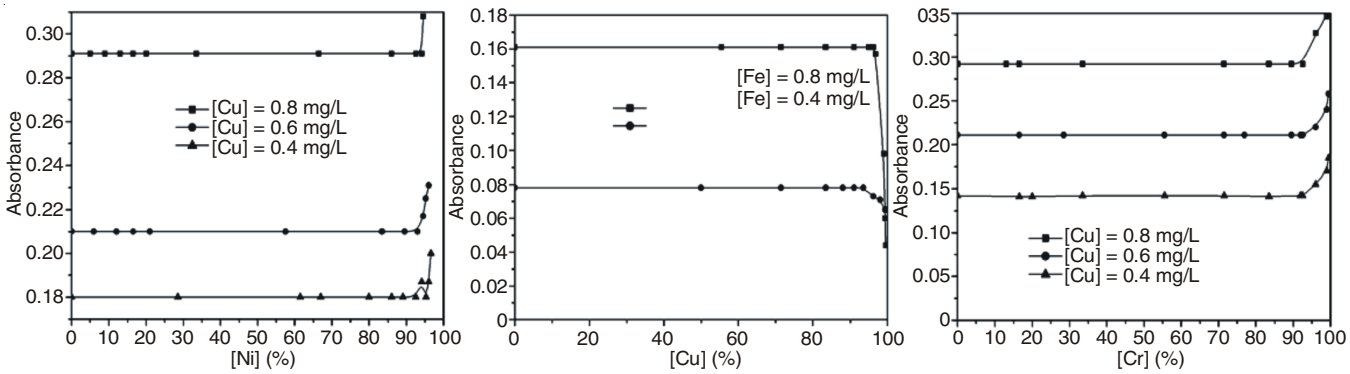

Fig. 2. Effect of metal ions on the absorption of solutions with different concentrations of the complex copper oxalyldihydrazide-acetaldehyde: (A) Nickel effect, (B) Iron effect, (C) Chromium effect

solution, λ_{max} = 445 nm, the molar absorptivity $\varepsilon = 1.5 \times 10^4$ mol $^{-1}$ cm $^{-1}$, the specific absorptivity a = 0.26 mL g^{-1} cm^{-1} and the detection limit of this method is 2 mg/L.

Effect of different cations on the determination of nickel: After the determination of λ_{max} (460 nm) and the calibration curve (0.2-2 mg/L of Ni^{II}) we have studied the influence of cations *i.e.*, Cr, Fe and Cu. A series of solutions of a fixed concentration of nickel is prepared and different percentages of studied cations are added. The absorbance is then measured at λ_{max} = 460 nm (Fig. 3).

Determination of chromium: The usual method for the determination of chromium is diphenylcarbazide method. This method is considered as the most sensitive and more selective compared to other methods such as chromate and EDTA methods. Diphenylcarbazide is the method used for the determination of chromium in iron, steel, ferroalloys, nickel, tin and other elements and in industrial water, biological materials, water, air and wood [6,7,12,13,31-34].

Method of diphenylcarbazide: In an acidic medium the diphenylcarbazide reacts with chromium(VI) giving a purple complex. This method can be applied to determine the chromium(III) after its oxidation in an acid environment using an oxidizing agent ($K_2S_2O_8$, H_2O_2). Since the absorbance of the solution varied with the acidic medium, it is necessary that the pH remains around 1 (optimum pH) by addition of sulfuric acid (0.05-0.1 M), in λ_{max} = 546 nm the molar absorptivity $\varepsilon = 4.17 \times 10^4$ mol $^{-1}$ cm $^{-1}$, specific absorptivity a = 0.80 mL g^{-1} cm^{-1} with a detection limit of 0.8 mg/L.

Effect of different cations on the determination of chromium: After the determination of λ_{max} (540 nm) and the calibration curve (0.01-0.2 mg/L of Cu^{II}) we have studied the effect of Ni, Fe and Cu. A series of solutions of the fixed concentration of chromium is prepared and different percentages of the studied cations are added. The absorbance is measured at λ_{max} = 540 nm (Fig. 4).

RESULTS AND DISCUSSION

From Fig. 1, it is worth noting that the nickel and chromium do not interfere during metering whatever their content in solution. The copper does not interfere in the test unless its amount is more than the amount of iron by 95 % and this is mainly because the copper(II) forms a non-coloured complex with the reagent.

From Fig. 2 we can infer that nickel does not affect unless its concentration is greater than 93 % with respect to copper. Chrome has an effect at a percentage more 93.5 %. Iron(III) does not affect the determination of copper, unless its percentage is more 95 %.

From the graphs in Fig. 3, it is noticed that the iron ions affect the determination of nickel if their amount is greater than the amount of nickel by 50 % and the same for chromium. Copper has no affect unless its concentration exceeds 87.5 %.

This interference is due to the formation of a coloured complex between the dimethylglyoxime and ions (Cu^{2+}, Fe^{2+}). We can avoid this interference by nickel-complex extraction with chloroform in an ammoniacal medium.

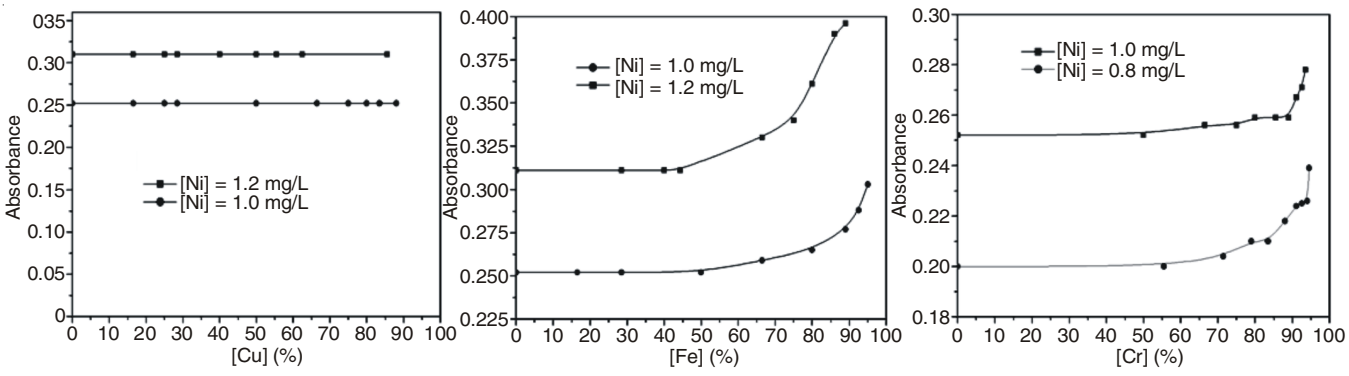

Fig. 3. Effect of metal ions on the absorption of solutions with different concentrations of the complex nickel(IV) dimethylglyoxime: (A) Copper effect, (B) Iron effect, (C) Chromium effect

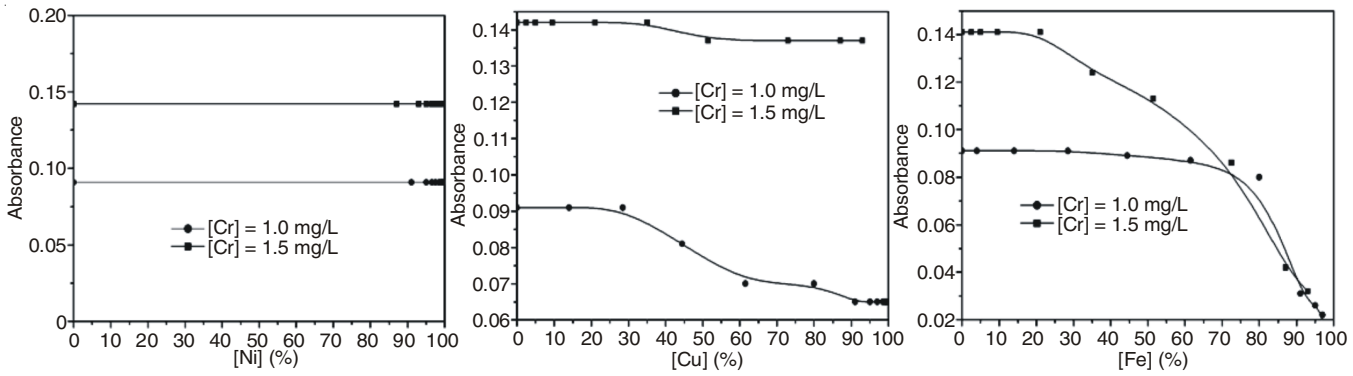

Fig. 4. Effect of metal ions on the absorption of solutions with different concentrations of the complex chromium(VI) diphenylcarbazide: (A) nickel effect, (B) copper effect, (C) iron effect

Fig. 4 showed that the nickel does not affect the determination of chromium. Iron(III) does not affect the determination of chromium, unless its content exceeds 20 %. Copper has an affect beyond 33 %.

To avoid these disabilities we must perform the separation of chrome from iron and copper using two ways:

Precipitation: The oxidation of Cr(III) to (CrO_4^{2-}) in alkaline medium and in the presence of an oxidizing agent and then precipitation of other ions.

Extraction with an organic solvent: Chromium can be extracted in small amounts from chlorohydric acid solution (1-3 mol/L) by a high selectivity separation method using methyl isobutyl ketone (MiBK). This method separates chromium for many elements such as: (Ni, Mn, Fe, V) [12].

Conclusion

To make a quantitative analysis of the different metals in sludge, we have used a simple, valuable and inexpensive method. In this paper we have opted the UV-visible spectrophotometry method. We applied this method for analysis of nickel, copper, iron and chromium. We studied the metal-metal interference. It was found that the quantitative determination of these wastes can be achieved provided that we follow a careful block diagram to avoid the possible interferences of a metal in the presence of other metals.

In the case of a mixture of hydroxides of Fe, Cr, Cu, Ni and according to the results of various interferences, it was obvious that, after total acid dissolution of metallic components

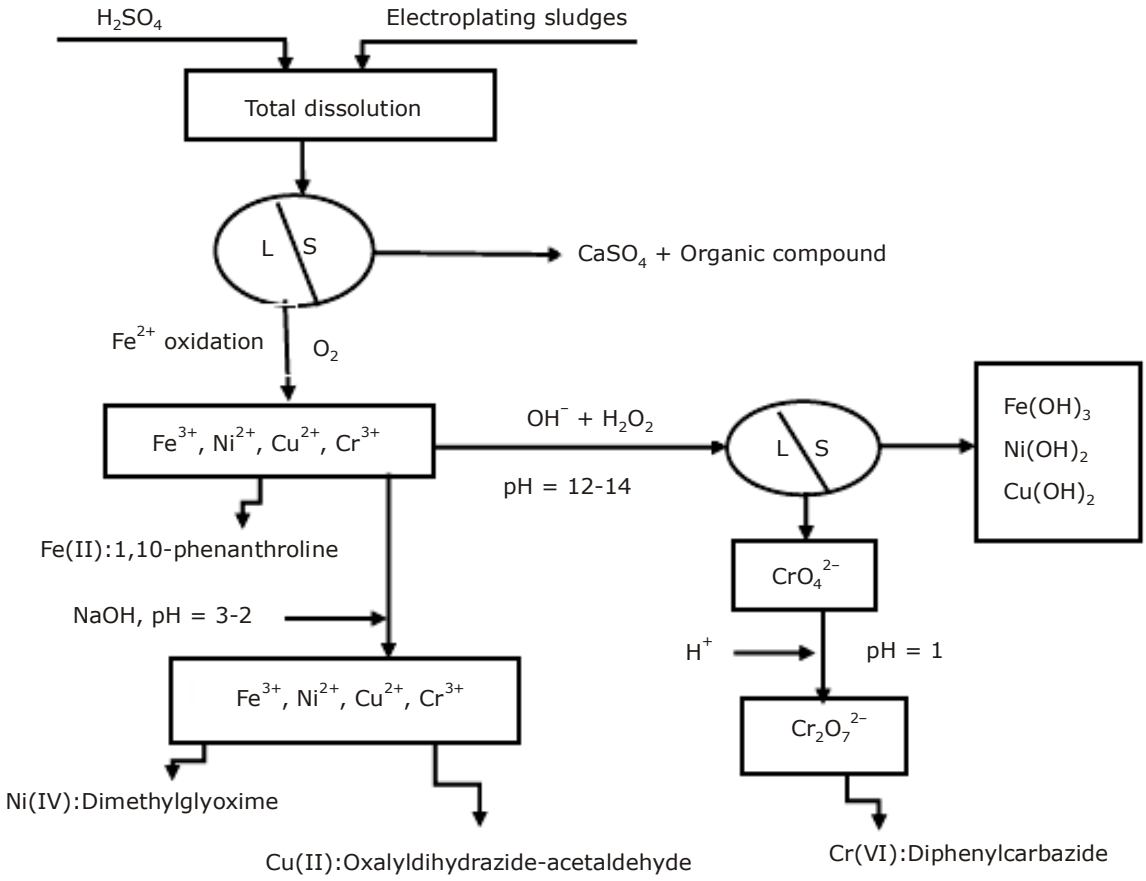

Fig. 5. Block Diagram of the proposed method for the analysis of a sample of electroplating sludges

of waste and filtration to separate solids we can undertake iron determination by 1,10-phenenthroline reagent since in this assay there is no influence of other metals, unless the amount of copper exceeds the amount of iron by more than 95 %. In this case, Cu(II) is blocked by thioglycolic acid and stripping the complex iron(II)-1,10-phenenthroline by *n*-octanol.

Then we take two samples of the solution:

In the first sample: We raise the value of pH to 2-3 to get rid of most of the iron(III) and chrome(III). In fact in solubility curves S = f (pH) of the cations mentioned above, at pH = 2-3 iron(III) and Cr(III) are less of about 50 % than nickel [14] and hence the nickel can be determined directly by using (dimethylglyoxime) reagent without any effect. The ratio of chromium(III) to the copper in all cases must be lower than 93.5 % of the copper. Hence, the copper can be determined by oxalyldihydrazide acetaldehyde reagent without any influence.

Second sample: The precipitation process is conducted in an alkaline medium (pH = 12-13) and in the presence of an oxidizing agent ($K_2S_2O_8$, H_2O_2) for separating the chromium as chromate (CrO_4^{2-}) which is determined by diphenylcarbazide reagent.

This suggested method used to determine the amount of minerals in the electroplating sludge (Fe, Ni, Cu, Cr), is illustrated by a block diagram as shown in Fig. 5.

Visible Spectrophotometry has been used to characterize easily and efficiently the sludges. It can predict possible metal-metal interference.

The electroplating sludges were originated from the industrial area of 'El alma', in Algeria, where a galvanization plant had previously operated. These sludges are classified F006 by the EPA. For example, Table-1 gives the mineral composition of four different sludges samples.

TABLE-1
MINERAL COMPOSITION OF FOUR DIFFERENT SAMPLES OF WASTE

Sample/metal	Cr(T) (%)	Fe(T) (%)	Cu (%)	Ni (%)
1	0.0720	6.74	3.990	13.98
2	0.0390	5.56	3.260	12.42
3	0.0028	5.03	1.400	8.59
4	0.0083	9.84	1.125	10.43

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