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by

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A New Spectrophotometric Method In Determination Of Molybdenum

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ABSTRACT

A new spectrophotometric method has been developed in determination of molybdenum by isoprophyl xanthate in weakly acidic media. The concentration limit of molybdenum by this method is 10^{-9} m/l.

INTRODUCTION

Molybdenum is one of the very important elements. It is used in the various branches of industries, including greasing and steel industry. Above all it plays an important role as catalyst in the plant and animal bodies [1], [2], [3], [4], [5]. Moreover in plant bodies it catalizes the fixation of atmosphoric nitrogen. The plants growing on the earths which are having no molybdenum, first fade and then rot. If, trace amounts of molybdenum is given to the same earths, plants grow well. Even by giving molybdic acid, as little as 30–50 grams per acre, to the barren earths, either the yield of crops or the nitrogen contents of the crops are increased [2].

At present, there are several methods to determine molybdenum [6], [7], [8], [9], [10]. But, still a more sensitive method, worthwhile to develope in order to determine it, because of its importance for plants and animals.

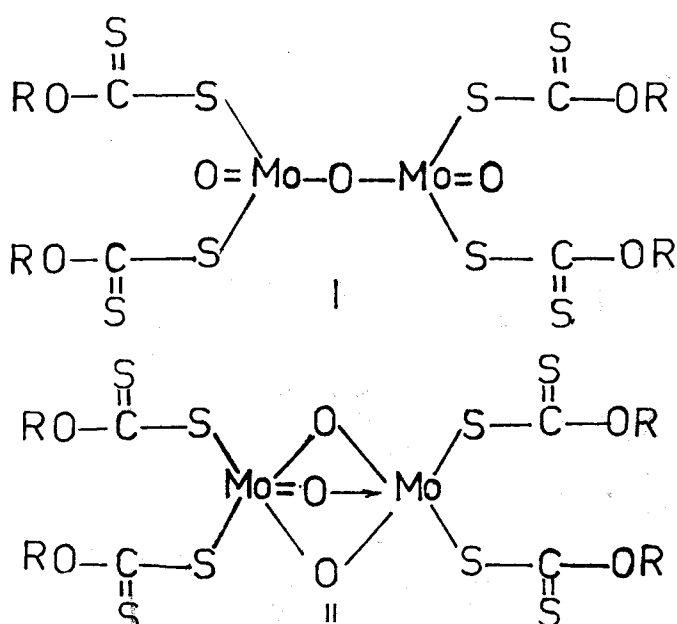
In this work we prepared a number of potassium xanthates and tried them to determine the molybdenum. Xanthates give dark purple coloured complexes with molybdates. Detectable concentration limits of molybdenum reached by these compounds have been given below.

Potassium	isopropylxanthate	10^{-9}	m/l,	Mo
”	isobutylxanthate	10^{-8}	”	”
”	Octylxanthate	10^{-7}	”	”
”	ethylxanthate	10^{-7}	”	”
”	amylxanthate	10^{-6}	”	”
”	tertiarybutylxanthate	10^{-6}	”	”
”	benzylxanthate	10^{-5}	”	”

Complexes form in aqueous media at about pH, 5. Complexes so formed in weakly acidic media, are extracted to chlorophorm phase. The colours of complexes in this phase are more intense than aqueous ones. As seen above, among the xanthates investigated, isopropylxanthate is the best in sensitivity, in order to determine molybdates. It is very nearly hundred times as sensitive as etlyl-xanthate which has been used for along time in spectrophotometric determination of molybdates.

All these complexes in choloroform or carbontetrachloride give a broad absorption band with a peak at about 520 mμ, Fig. 1.

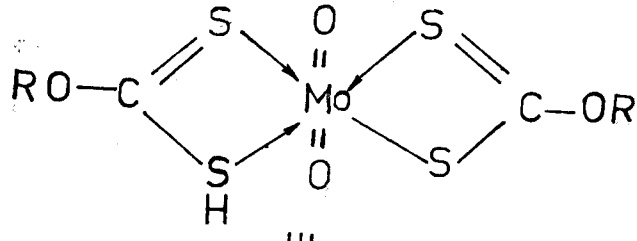
The formula of the complexes are not fully enlightened. Some of the proposed formulae are as follows (I, II), [11].



(R, stands for alkyl groups as, ethyl isopropyl etc)

We have done some magnatic susseptibility measurements, by taking into accounts the Pascal Constants as well. Unfortunately the results have supported non of the formula. Because, free electron calculated by this way, change from 0,15–0,84 per formula or per two atoms of molybdenum.

Molecular weights determined by cryoscopic method have supported both formulae.



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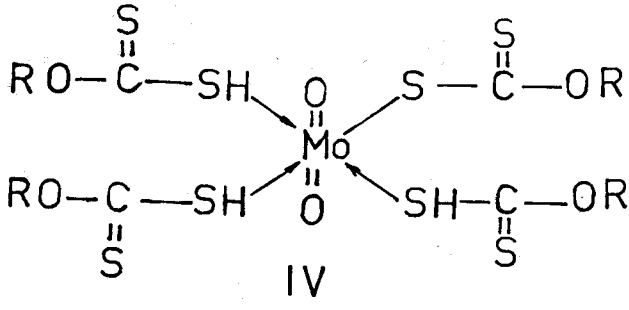

IV

Job's continuous variation method has shown two maxima. First one, corresponds to the ratio of molybdate to xanthate 1:2, the second one, corresponds to the ratio of molybdate to xanthate 1:1. First maximum is in accordance with the cryoscopic data. The second one is probably due to formation of trace amounts of molybdenum V complexes with a very big molecular extinction coefficients (ε). This complex is probably due to for-

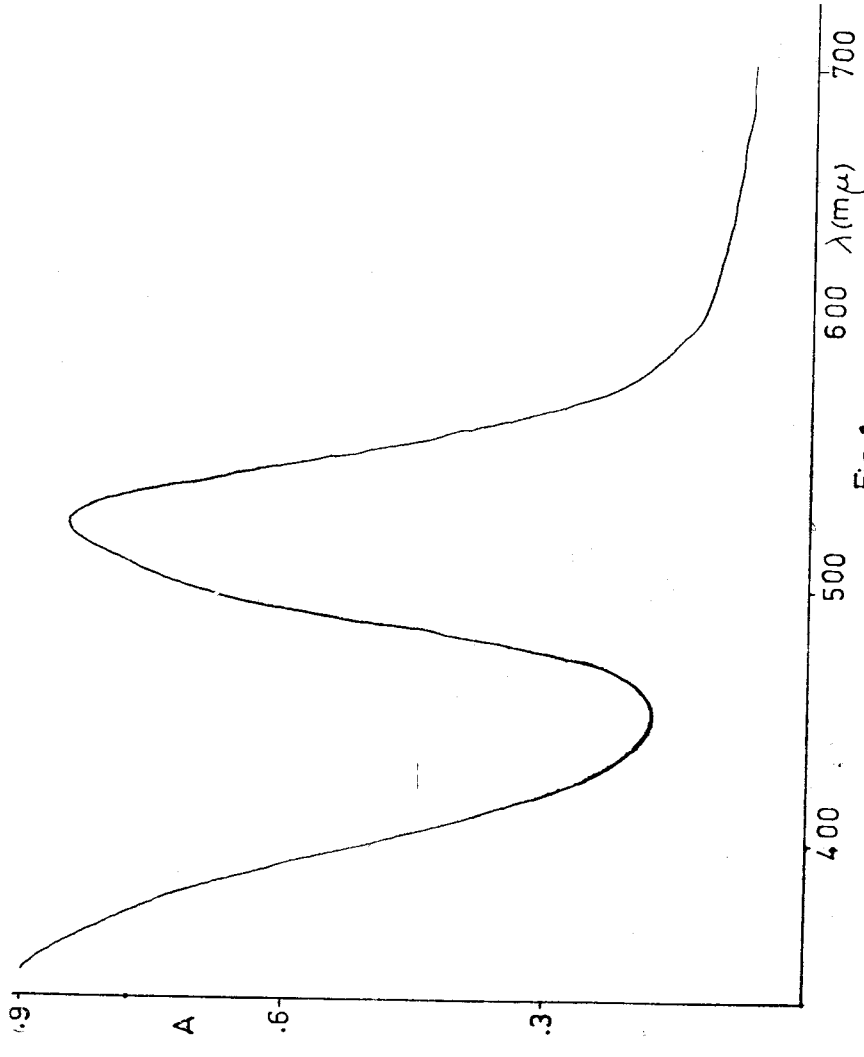

Fig. 1

mation of new complexes III, IV. Molybdenum VI is easily partially reduced to molybdenum V (molybdenum bleu). The strength of the absorption of the second complex is very nearly the same as the first one, Fig. 2.

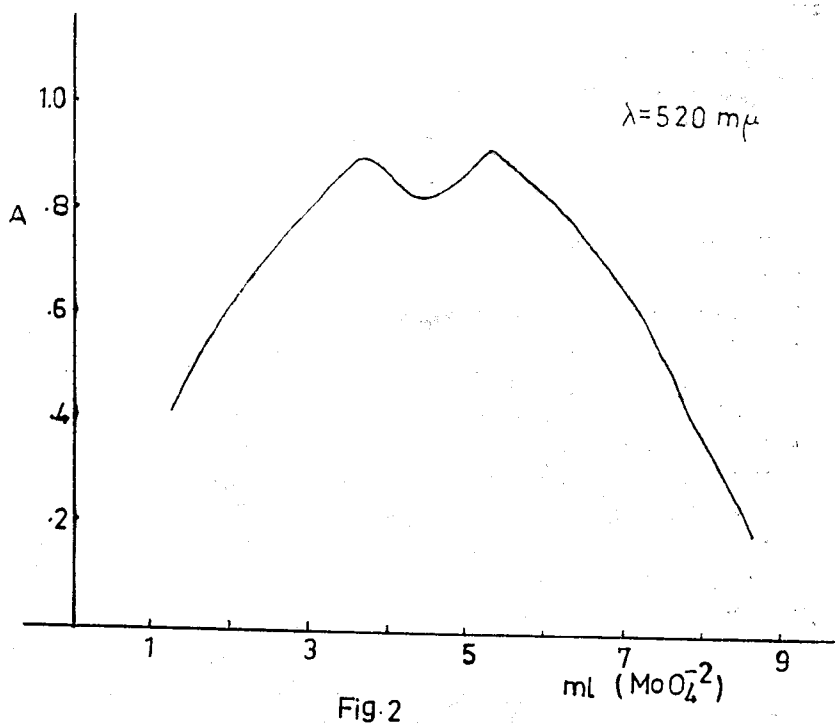

Fig. 2

EXPERIMENTAL

Potassium xanthates have been obtained by usual method: 150 grams of potassium hydroxide (2,7 mol) is dissolved in 1,5 liter of pure ethyl alcohol. Onto the solution, 230 grams of carbondisulfide (2,9 mol) is added drop by drop. While the addition of carbondisulfide, the solution is stirred vigorously and temperature is kept under 10 °C, by cooling the reaction vessel with ice-water mixture. Crystalline yellow ethylxanthate is filtered by vacuum and then is washed with alcohol.

The other xanthates have been obtained by the same method.

In order to keep pH round about 5 within the formation of complexes, a series of buffers have been prepared and used.

Magnetic susseptibility measurements have been made on a Gouy type magnetic balance, containing a very powerful electromagnet (up to 22000 gauss).

Spectrophotometric data have been obtained by a Beckman DU type UV spectrophotometer.

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ÖZET

Yeni geliştirilen bu spektrofotometrik metotla zayıfça asitli ortamlarda, konsantrasyonu litrede 10^{-9} mola kadar olan molibdenin isopropilksantogonatla tayin edilebileceği gösterilmiştir.

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