

Spectrophotometric Analysis of Cobalt and Nickel Examined by Exchange Extraction Separation Method

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Abstract

The demand for the recovery of valuable metals in the need to understand the impact of heavy metals in the environment on human life led to the development of new method for the extraction and recovery and analysis of metal ions. Gindin et al examined the extraction of metals by long aliphatic fatty acids. It has been proved experimentally that when a metal is in organic phase as a salt of fatty acid (a soap) and another in the aqueous phase as a salt of a mineral acid there is an exchange reaction by which bivalent metals can be extracted. This paper deals with the exchange extractions separation of metals by distribution of soaps which is a unique hydrolytic methods which differs from other hydrolytic method in which precipitates are formed.

Keywords: Trace Elements, Extraction, PAR, Atomic Absorption Spectrometry, Molar Ratio.

Introduction

The process connected with the distribution of corresponding soaps in the mono and bivalent metal into aqueous and organic phase depends on the basicity of metal ion and the activity products of the hydroxide or the corresponding basic salts. The distribution of fatty acid soaps into aqueous and organic phase depends upon the basicity of the metal ion and solubility product of corresponding derivative. Therefore extraction of metals by fatty acids in organic phase could be considered as useful procedure for the separation of metals in microgram quantities. This procedure could be developed for larger quantities which could be significant because of easily and cheap availability of fatty acid extrants in comparison to other organic chelating agents. Basically it is known that Lanthanide can be extracted quantitative at pH 4.0 to 5.5 by solution of n-butyric acid in chloroform. In view of advantages and report of an investigation described earlier the extraction of metals such as Mg, Mn, Co, Ni, Cu, Cd, La, Pr, Nd, Eu, Tb from aqueous solution of stearic acid into polycrystalline naphthalene was taken during the course of present studies.

Factors Affecting Extraction

There are many factors like pH, Reagent concentration, amount of extracting agents which affect the absorption of metal chelates on the solid polycrystalline material. The mechanism of phenomenon of adsorption of metal chelates on solid material is not understood at all, but the nature of metal chelates and its insolubility in aqueous phase can be considered as most important factor. Therefore the composition of the complexes extracted from the aqueous solution has been evaluated from extractive spectrophotometric determination data. Both the Job's method of continuous variation and the mole ratio method have been used and the results obtained are indicative of the formation of complex derivative between Metal Ions and Reagent indefinite molar ratio.

Azo Dyes

The Azo Dyes have always been considered very sensitive spectrophotometric agents. 4-(2-Pyridylazo)-resorcinol (PAR) was first prepared by Chichibabin by coupling resorcinol with sodium 2-Pyridylidiazotate. Originally the conditions used in recent preparation the use of carbon dioxide is dispensed with and the dyes obtained as monosodium or disodium salt. Sodium salt are more water soluble than the free die itself, and are preferentially used in analysis for this reason. The



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aqueous solutions are orange. The dye as a sodium salt is soluble in acid and alkaline solution and to a lesser extent in alcohol. It is insoluble in ether. PAR forms intensely coloured complexes with many metals (transition and inner transition) ions and is widely used in analytical chemistry. The soap extracts were treated with HCl : HNO₃ (1:5 volume ratio) and extracted in aqueous solution and determined with PR spectrophotometrically The molar ratio in the reactions of rare earth metals and PAR was determined by the method of continuous variation as well as by the mole ratio method studies

Cobalt Carboxylate

Cobalt formate $C_2H_2CoO_4$ is isostructural with the Nickel and copper formates in which the Carboxylates group behaves as a bridging group giving rise to polymeric species as reported by Ancyskina. It has been shown by x-ray structural studies that Cobalt Acetate dihydrate $Co(C_2H_3O_2)_2$ contains Uni dentate Acetate groups which are strongly hydrogen bonded to a coordinated water molecule. The electronic spectra and magnetic properties of a number of mononuclear and polynuclear complexes of Cobalt carboxylates with pyridine and heterocyclic base have been reported by Lever, Drew, Catt rick and Manhas the complex indicates that it contains Cobalt in 6 co-ordinate geometry with tetragonal splitting

Nickel Carboxylate

Kogmann has shown that format $Ni(O_2CH)_2 \cdot 2H_2O$ has two different kinds of octahedral nickel atoms one of those are surrounded by six format oxygen atoms while the other octahedron is completed by 4 water oxygen atoms. The metal atoms are linked by format bridges forming an infinite polymer.

Importance

Metal carboxylates having moderate stability and high-lability are useful reagent for commercial synthesis of organic compounds .A large number of metal carboxylates find application in biological aspect. The metal carboxylate of long chain fatty acids are the most important derivative industrially .Wide variety of metal carboxylate find important application number of industries viz. Soap, textile, paper ,cement etc. Carboxylates of Na, K, Mg, Ca, Ba, Zn, Al, Sn. Pb, Mn, Fe, Co, Ni, Cu have generally been commercially employed in these industries. Their appreciable solubility in organic solvents (except Sodium and potassium salts) have been reported of Markley and availability of reasonable cost make them potentially useful as waterproofing materials etc.

Aim of the Study

Extraction of Transition and Inner Transition Metal Soaps

The organic derivatives of metal or metal carboxylate are commonly known as soaps .Metallic soaps are there for simple carboxylate of alkaline earth or other polyvalent metals with general formula $M(O_2CR)_n$ where M is a metal in oxidation state (II) or(III) n and R is an organic radical containing at least 6 to 7 carbon atoms. The term metallic soaps is restricted by some to salts of fatty acids that is those in which R is an aliphatic radical also in its broad

sense the term also includes source of certain cyclic acids. Little work has been done in this area major interest centred on long chain aliphatic Carboxylic acids as extractants in a recent survey presented by Fletcher and Flett. It should be noted however that the dimerization of the carboxylic acid is a well established fact so that the expression for the letter should be (R_2H_2) org and the extracted species is invariably solvated with one or two acid molecules Futhermore the metal carboxylate in the organic phase tends to polymerize with increase in metal concentration. Thus extraction of Copper Nickel and Cobalt with naphthenic acid benzene gives the extracted species Cu_2R_4RH , Ni_2R_4RH and Co_2R_4RHR respectively.

Methodology

Exchange Extraction of Metal Soaps

Thus metal can be effectively separated from the aqueous phase extraction involving exchange reaction between their organic acid salt (soaps) into an organic phase. It was found that copper precipitated as carbonate or Hydroxide it completely extracted into a solution of butyric and certain other higher acids in the Ethyl Acetate or benzene. Gindin et al further proved experimentally that when a metal is in organic phase is a salt of fatty acid(a soap) and other in aqueous phase as a salt of mineral acid there is an exchange reaction .

Dissociation of Soaps in Aqueous

Long chain of fatty acid is hydrophobic and the soaps are soluble in water to very small extent. However it is assumed that the soaps are dissociated in water (but not is organic phase) their distribution will depend on the basic properties of the metal the more basic is the metal greater will be the solubility of its soap in the water. It is expected if the pH of aqueous phase is increase the concentration of soap rises. The exchange extraction separation of metal is therefore a unique hydrolytic method which differs from the usual hydrolytic method in the way that precipitates are not formed and consequently there is no occlusion of the metal which is being separated by the solid phase. It is also easy to achieve multiple stage separation in a counter current column, exchange extraction. In conclusion extraction of metals by long chain aliphatic acids allows the separation of metal with very similar properties for example Cobalt and Nickel which is not possible by hydrolytic precipitation.

Preparation of Stock Solution

Magnesium Sulphate Solution: - Magnesium sulphate solution prepared by dissolving requisite quantity of an analar sample in double distilled water. The Magnesium Content was determined by standard EDTA solution in Ferrochrome Black T as indicator.

Cobalt Nitrate Solution

The Cobalt nitrate solution was prepared by dissolving requisite quantity of analar samples in double distilled water. The strength of the solution was determined by titration with EDTA solution using Xylenol orange as indicator as described by Vogel.

Chelating Reagents**Fatty Acid (Stearic Acid)**

Stearic Acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) pure sample (EMerck) was dissolved in ethyl alcohol diluted to 100 ml in volumetric flask with absolute alcohol. Its strength was determined by titration with alcoholic water solution 80:20 of NaOH in presence of phenolphthalein as indicator

Distribution of Metal Soaps during Exchange Extraction by Polycrystalline Naphthalene

Extraction of metal salts of aliphatic acids is closely related to the distribution of the soap between the organic and aqueous phases. In the extraction by aliphatic acids in the presence of alkali the equilibrium is determined by the combined distribution of the acid and the soap of the metal. In the studies reported on distribution of metals during the exchange extraction between aqueous phase and organic phase consisting of 400 gram per litre solution of aliphatic acid in kerosene was reported by Bugaeva et al. These workers employed organic fatty acid containing C7 to C9 fraction with average molecular weight 142 determined by titration with alcoholic alkali. The solution of soaps in the organic phase was prepared as follows; the carbonates or occasionally Hydroxide with precipitated from the Aqueousulfates or chloride leaving 5-7% of the metal in solution. The precipitate was filtered off washed thoroughly with water dissolved in the organic phase and the aqueous layer separated. The metal in the organic solution of the show was determined. The solution was measured, with a burette, into a graduated glass cylinder and made up to the 50 ml with aliphatic acid of the appropriate concentration kerosene. 50 ml of distilled water were then added and the mixture was shaken for 10 minutes the layers were separated and the aqueous phase was analysed for the sodium soaps. In the organic phase was shaken with an excess of aqueous. The copper soap solution formed was extracted in the usual way, and the copper determined. The aqueous phase was analysed by one of two methods: 1. Titration with HCl in the presence of methyl alcohol 2. determination of R ion by treating the aqueous phase with the aliphatic acid in kerosene adding an excess of CuSO_4 shaking and extracting the copper from organic phase and determining it iodometrically.

From the studies it is evident that when the solution of the sodium soaps is added to the aqueous solution of metals salts the exchange reaction is quantitative and the metal soap of transition metal ions are extracted into the aqueous phase quantitatively. However the procedure is tedious and required a considerable period of time of 10 minutes to reach the equilibrium therefore in the studies pertaining to the distribution of metal salts of few transition and inner transition metal ions and between the aqueous and solid organic phase (polycrystalline) was modified. The metal soaps were precipitated from the aqueous solution by addition of alcoholic solution of sodium stearate and after the complete precipitation of metal salt metals soaps this solution and the precipitate was mechanically shaken on a magnetic stirring for 2 hours for attainment of

equilibrium. Thereafter the transition metal or inner transition metal soaps extracted by addition of 2 gm of naphthalene in 10 ml of acetone, in accordance with the general understanding about the solid liquid extraction. The microcrystalline naphthalene precipitated extracts the precipitate of metals soaps into itself quantitatively. Therefore in these reported praseodymium/ Neodymium/Cobalt/ Nickel/Copper ions were extracted after formation of carboxylate or soaps using microcrystalline naphthalene as an extract.

Stearate is prepared by dissolving the stearic acid in alcoholic solution of sodium hydroxide in 1: 1 molar ratio was added to the above solution. The requisite volume of distilled water was added up to 50 ml. The precipitate of the metal soaps in aqueous phase was stirred for 2 hours for equilibrium action as mentioned earlier. A 2.0 gm portion of polycrystalline naphthalene in 10 ml of acetone was added. The content of the flask was heated and steered for 1 hour thereafter then contents were allowed to stand and cool for 2 hours till the solid microcrystalline neck clean solidified. Again a 50 ml of distilled water was added for complete precipitation of the organic extractions the compact mass of solidified naphthalene so obtained was filtered through a sintered glass filter specially designed for this purpose. The Residue and the precipitate was washed several time with cold water and finally dried at room temperature with the help of an aspirator. The metal was Re extracted from the solid Residue by a threefold treatment with mineral acid (1:5 HCL, H_2SO_4 , HNO_3). The solution was heated as soon as the solid naphthalene melted completely again then the solution was stirred vigorously after a few minutes and 20 ml distilled water was added to above. The Re extraction process was repeated twice separate the acid and naphthalene from the organic phase. The aqueous phase now containing the metal salt was separated from organic Phase (Naphthalene and stearic acid) by filtering through a sintered glass filter. The filtrate containing the metal salts was heated to dryness and redissolved in distilled water then transferred in 50 ml flask it was diluted to 10 ml with double distilled water. Its pH was adjusted with dilute Ammonia and acetic acid solution in the complexing reagent solution was added and exactly 10 ml solution was made in a volumetric flask with double distilled water the mixture was allowed to stand for 30 minutes for equilibrium and the portion of it was taken in a quartz photometric cell. Optical density was measured against Reagent blank solution. The metal Ion concentration was determined by UV visible spectrophotometer. Atomic absorption spectrometry was used for determination of Cobalt and Nickel.

Spectrophotometric Determination Jobs Continuous Variation Method

This method was introduced by job in modified by Vosburgh and Cooper to determine the composition of the complex. The principal of the method lies in the determination of absorbance of solution containing different ratios of metal ion solution and the ligand solution, the total volume being kept constant. A graph is drawn between the

volume of fraction ($V_m/V_m + V_r$) and the absorbance. The curves obtained as a parabola. The point of intersection of the two straight lines drawn from both the ends of the curve corresponds to the composition of the complex. Job's method gives satisfactory result for several complexes instance of inconclusive result have been reported by Dewi, Job and Minler. This method is not applicable when more than one complex is formed in the concentration range of study. However Cooper et al reported that this method is still useful if a slightly modified procedure is followed. The modified procedure consist in first ascertaining whether or not any only one complex is formed. The metal and ligand solution for this purpose for the same concentration and mixed together in simple integral volume ratio and absorption spectrum of each mixture is recorded. If the absorbance attained is maximum at the same wavelength in each case, can be assumed that a single complex is formed. The job Method can successfully be employed for determination of composition of complex

Extraction of Metal Stearates

The metal salts formed in the aqueous phase in the above reaction are absorbed on polycrystalline naphthalene. The equilibrium is attained after stirring amount of metal absorbed on naphthalene were re extracted with the help of a solution mixture of HCl and HNO_3 in volume ratio 1:5. This acid mixture is found to be more suitable for Re extraction of metals from soap absorbates in naphthalene.

The qualitative test for each metal ions were performed for their presence in the naphthalene absorbates treated with acid mixture. It shows absence of metal components in organic phase after Re extraction. These tests were negative for each of the metal ion tested. Gindin et al have reported that the re extraction of metal soaps from kerosene is achieved stoichiometrically with the above-mentioned acid mixture (HCL + HNO_3) The concentration of the metals of extracted were determined in re extractants 1. Complexometrically and 2. Spectrophotometrically.

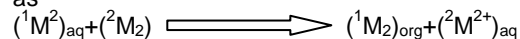
Results and Discussions

Equimolar (1×10^{-4}) solutions of Cobalt and Nickel with 4(2-Pyridylazo) resorcinol are taken in different volume ratios in a set of 10ml standard flask keeping the total volume of metal and PAR solutions at 5ml with 3ml of buffer solution and adjusted the pH. Cobalt pH8.0 and Nickel pH9.5 and the contents diluted to the volume with distilled water. The absorbance of the resulting solution is measured for Cobalt at 510nm and Nickel at 494nm. Job's curve is constructed by plotting the absorbance against volume ratio i.e. $V_m/V_m + V_r$. The resulting graph is shown and is clear that the composition of the complex is 1:2[M:R]

Conclusion

Gindin et al examined the extraction of metals by long chain aliphatic fatty acid. It has been

proved experimentally that when a metal is in organic phase as a salt of a fatty acid (a soap) and another in the aqueous phase a salt of a mineral acid, there is an exchange reaction by which bivalent metals can be extracted. The exchange reaction can be represented as



On the basis of the results for the exchange reaction of a Cobalt soap CoR_2 with $CoSO_4$. A complete analogy has been established between the behaviour of metals in the above-mentioned exchange reaction and in exchange extraction by alkali hydroxide. The distribution of corresponding soaps in the mono and bivalent metal into aqueous and organic phase in the reaction depends on the basicity of metal ion in the activity products of the Hydroxide or corresponding basic salts. The exchange extraction separation of metal by distribution of soaps is therefore a unique hydrolytic method which differs from the other hydrolytic method in which precipitates are formed consequently there is no known occlusion of the metal being separated into solid phase. The bivalent and trivalent metal form soaps with stearic Acid which are highly insoluble in water given to the lyophobic character of the aliphatic chain of the carboxylic acid. The Carboxylic group of these aliphatic acids for metal soaps with bivalent and trivalent ions in the alkaline region of the pH. The distribution of metal source of few transition and inner transition metal ions between the aqueous solid or any phase polycrystalline naphthalene. The metal soaps were precipitated from the aqueous solution by the addition of alcoholic solution of sodium stearate. After the complete precipitation of metals of the solution was mechanically shaken on a magnetic stirrer for 2 hours for attainment of equilibrium. Thereafter the transition and inner transition metal were extracted by addition of 2.0 gm of naphthalene and 10 ml of acetone the compact mass of solid liquid naphthalene was so obtained was filtered through a sintered glass filter specially designed for the purpose. The Residue on precipitate was washed several times with cold water and finally dried at room temperature by aspiration with the help of water pump attached to filtration assembly. The metal were reextracted from the solid residue or precipitate from the organic phase by 34 treatment with mineral acid one is to 5 volume ratio of HCL H_2SO_4 and HNO_3 the extraction process was repeated twice the filtrate solution containing the metals all were heated up to dryness in Re dissolved in distilled water then transfer into flask after adjusting PS the complexing agent POS solution was added it was allowed to stand for 30 minutes for equilibrium and its optical density was measured spectrophotometrically.

Job's method of continuous variation concentration of Stock solution, PAR and cobalt

Volume of Co ^(II) solution in ml V _M	Volume of PAR solution in ml V _R	Volume ratio V _M /V _M +V _R	Absorbance
0.50	4.50	0.10	0.205
0.75	4.25	0.15	0.320
1.00	4.00	0.20	0.405
1.25	3.75	0.25	0.470
1.50	3.50	0.30	0.485
1.75	3.25	0.35	0.475
2.00	3.00	0.40	0.440
2.25	2.75	0.45	0.410
2.50	2.50	0.50	0.365
3.00	2.00	0.60	0.280
3.50	1.50	0.70	0.200
4.00	1.00	0.80	0.130
4.50	0.50	0.90	0.070

Co^(II) - 1.0 × 10⁻⁴ M
 PAR - 1.0 × 10⁻⁴ M
 pH = 8.00
 Reference - Deionised water

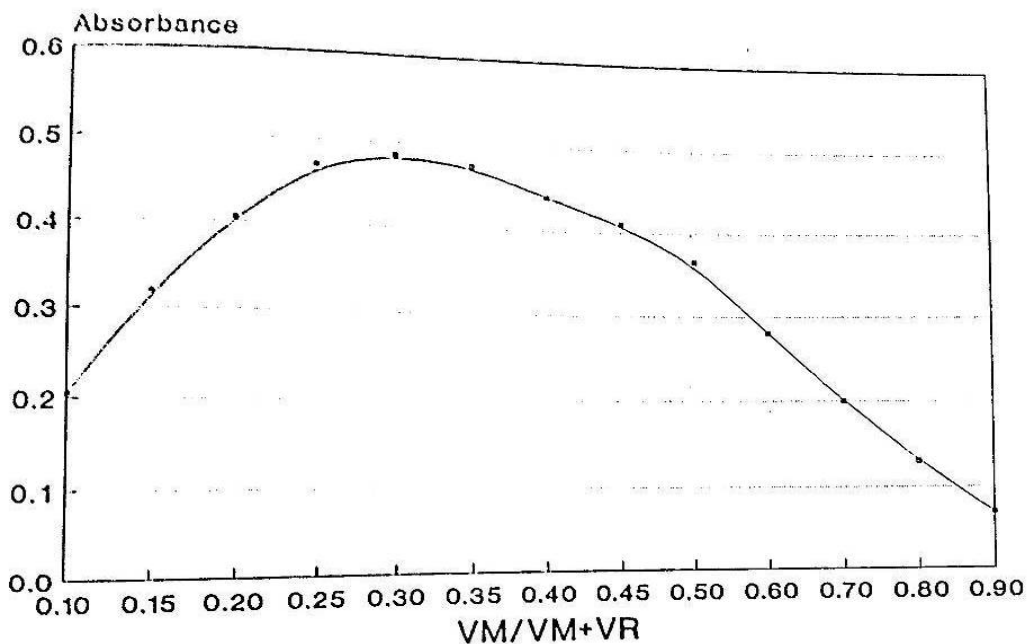


Fig. 4.2.23 Job's Curve

Co^(II) - 1.0 × 10⁻⁴ M
 PAR - 1.0 × 10⁻⁴ M
 λ max 510 nm
 pH - 8.00
 Reference - Deionised water

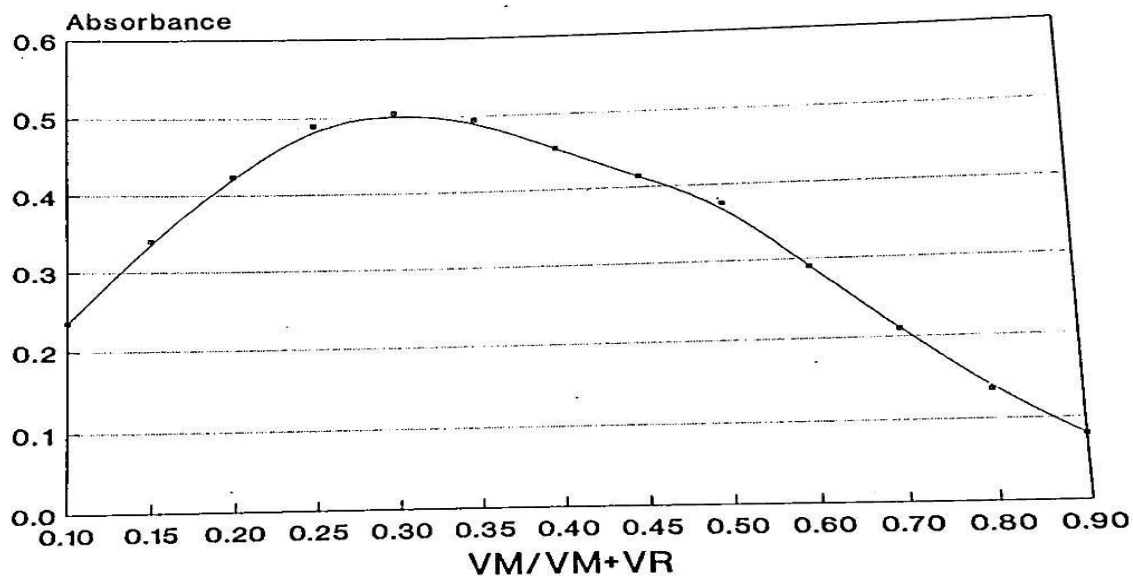


Fig. 4.2.24 Job's Curve

Ni^(II) - 1.0 10⁻⁴ M
 PAR - 1.0 x 10⁻⁴ M
 λ max 494 nm
 pH - 9.50
 Reference - Deionised water

Job's method of continuous variation concentration of Stock solution, PAR and Nickel

Volume of Ni ^(II) solution in ml V _M	Volume of PAR solution in ml V _R	Volume ratio V _M /V _M +V _R	Absorbance
0.50	4.50	0.10	0.235
0.75	4.25	0.15	0.340
1.00	4.00	0.20	0.425
1.25	3.75	0.25	0.490
1.50	3.50	0.30	0.505
1.75	3.25	0.35	0.495
2.00	3.00	0.40	0.455
2.25	2.75	0.45	0.415
2.50	2.50	0.50	0.375
3.00	2.00	0.60	0.290
3.50	1.50	0.70	0.210
4.00	1.00	0.80	0.135
4.50	0.50	0.90	0.080

Ni^(II) - 1.0 x 10⁻⁴ M
 PAR - 1.0 x 10⁻⁴ M
 pH = 9.50
 Reference - Deionised water

Absorbance vs. wave length data for Cobalt/Nickel/Copper-stearate into poly crystalline naphthalene from aqueous phase.

Wave length (nm)	Co ^(II) -PAR	Absorbance Ni ^(II) -PAR	Cu ^(II) -PAR
450	0.105	0.065	0.050
460	0.145	0.135	0.095
470	0.200	0.260	0.140
480	0.265	0.335	0.180
490	0.340	0.405	0.235
494	0.365	0.415	0.245
500	0.395	0.400	0.290
510	0.425	0.380	0.340
520	0.405	0.325	0.375
525	0.380	0.290	0.380
530	0.355	0.250	0.340
540	0.270	0.160	0.215
550	0.175	0.110	0.140
560	0.120	0.070	0.075
570	0.055	0.035	0.040
580	0.020	0.015	0.020
590	0.010	0.010	0.015
600	0.005	0.010	0.010

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