Recovery of indium from etching wastewater using supercritical carbon dioxide extraction

Hui-Ming Liu [a,b,*], Chia-Chan Wu [a], Yun-Hua Lin [b], Chien-Kai Chiang [b]

[a] *Institute of Occupational Safety and Hazard Prevention, Hungkuang University, Shalu, Taichung Hsien, 433, Taiwan, ROC*
[b] *Department of Safety, Health and Environmental Engineering, Hungkuang University, Shalu, Taichung Hsien, 433, Taiwan, ROC*

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ABSTRACT

This study presents supercritical carbon dioxide ($scCO_2$) extraction as an inherently safer and cleaner method for the recovery of indium (In) from the real etching wastewater obtained from indium tin oxide (ITO) etching process. Efficient chelation-supercritical fluids extraction (SFE) from etching wastewater was obtained at 80 °C, a pressure of 20.7 MPa, and with 15 min static extractions followed by 15 min dynamic extraction. The extractions were performed using unmodified $scCO_2$ in the presence of the fluorinated β-diketone chelating agent, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (HFOD). Percentages of indium recovery from etching wastewater were between 90.8% and 100.3% ($n = 6$) with relative standard deviations of <10%. The accuracy of the procedure was confirmed by determining indium levels in a single element standard solution. The developed method was applied to the analysis of real etching wastewater samples as well as to a commercially available ITO etching reagent (ITO-06SD) with satisfactory results.

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1. Introduction

Flat panel displays (FPD) manufacturing is one of the largest applications of indium (In), and consumes over 70% of the world's annual indium output [1]. Indium tin oxide (ITO) is frequently used as a conductive transparent coating in FPD devices, such as thin-film transistor liquid crystal displays (TFT-LCDs), plasma display devices, and field emission devices. Targets of ITO are commonly sputtered on glass panels, wherein less than 30% of the indium is transported from the target to the glass panels, resulting in large quantities of residual indium generated by the cleaning/etching of glass surfaces. Recently, indium is also used in synthesis of compounds such as indium phosphide (In_2P_3) and indium chloride ($InCl_3$). These indium compounds are important new materials in the semiconductor industry due to their superior conductivity when compared to silicon-based materials. Accordingly, the demand for indium has increased in recent years as a result of its application as a semiconducting material and as a transparent conducting material in TFT-LCDs manufacturing. Unfortunately, indium is distributed in the earth's crust at low concentrations. For example, trace amounts of indium can usually be found with sphalerite (ZnS) ores, and are primarily obtained as a by-product of zinc mining [2]. As current indium metal consumption rates, the global reserves of indium metal are estimated to only last for another 20 more years. Therefore, there is a growing interest in the development of new indium metal recovery methods [3].

It is worth mentioning that exposure to some nearly insoluble indium compounds in ITO manufacturing and recycling plants poses a risk for interstitial lung damage [4]. As of now, limited information is available describing the environmental impact of indium, but it is known that exposure to these indium compounds induces cytotoxicity in some animal experiments [5]. Hence, it is necessary to develop an inherently safer and cleaner procedure for the recovery of indium.

Several studies have applied many methods to recovery of metals from liquid waste matrices including liquid–liquid extraction (LLE) [6], ion-exchange [7], co-precipitation [8], solid phase extraction [9] and electroanalytical techniques [10,11]. The main disadvantage of the liquid–liquid extraction process is related to the loss of extractant resulting from its partial dissolution in the aqueous phase, which may result in environmental hazards and economic limitations. Ion-exchange technology also has several disadvantages such as slow adsorption and desorption rates, poor selectivity and a requirement of concentrated electrolytes for desorption. The other aforementioned indium recovery methods are laborious and time-consuming, and result in the use and release of excessive amount of hazardous solvents, a high solvent recovery cost, and may pose environmental and health hazards. On the

* Corresponding author at: Department of Safety, Health and Environmental Engineering, Hungkuang University, Shalu, Taichung Hsien, 433, Taiwan, ROC.
Tel.: +886 04 26318652x4013; fax: +886 04 26319175.
E-mail address: hmliu@sunrise.hk.edu.tw (H.-M. Liu).

other hand, the low critical temperature (31.3 °C), moderate critical pressure (7 MPa), non-toxicity, and low cost of CO_2 make supercritical fluids extraction (SFE) an attractive alternative to conventional sample pretreatment methods for the extraction and recovery of metal ions and organometallic compounds from liquid and solid samples [12,13]. Nevertheless, direct extraction of metal ions by $scCO_2$ is inefficient because of the charge neutralization requirements and weak solute–solvent interaction. Spiking $scCO_2$ with a suitable chelating agent increases the solubility of metal ions in $scCO_2$. Consequently, chelation-SFE is a promising approach for treating metal-contaminated materials and recovering metal ions from waste materials [14].

A variety of organic chelating agents, such as crown ethers, dithiocarbamates, β-diketones, tributyl phosphates, and phosphoric acid derivatives, have been used for SFE of metal ions from various matrices [15–18]. Meanwhile, acetylacetone (ACAC) is commonly used as a chelating agent in the SFE of metals due to its ease of complex formation, high solubility, and the thermal stability of the metal complexes it forms. In 1992, Dr. Wai and co-workers first investigated the extraction of metal ions from a liquid solution using $scCO_2$ and acetylacetone as a chelating agent with *in situ* chelation [19]; however, metal acetylacetone complexes are often poorly extracted from aqueous solutions because mass transport between hydrophobic chelating agents and hydrophilic metal ions is limited. This problem can be overcome by using fluorinated agents, such as fluoroether and fluoroalkyl, which are hydrophilic. Fluorinated chelating agents are effective because of their high stability in supercritical fluids, and the solubility of the acetylacetone chelating agent is increased by several orders of magnitude after substituting of hydrogen atoms for fluorine atoms [20].

Application of SFE to recovery of metals from liquid matrices is usually hindered by poor mass transport [21]. To the best of our knowledge, no effective and commercially available chelating agent has yet been reported for the $scCO_2$ extraction of indium from etching wastewater. The quantitative recovery of In(III) ions from acidic aqueous solutions using piperidinyldithiocarbamic acid and 2-thiopyridine as chelating agents was reported recently [22]. In the paper, the authors focused on the quantitative recovery of In(III) ions from acidic aqueous solution, and not from real etching wastewater. Moreover, piperidinyldithiocarbamic acid is not commercially available and its routine use is limited by the cost associated with its synthesis in small quantities. 2-Thiopyridine is an irritant to the skin, eyes, and respiratory system. Therefore, the purpose of this study is to investigate the feasibility of indium recovery from real wastewater form ITO etching process by $scCO_2$ extraction with a commercial fluorinated agent and subsequent measurement by flame atomic absorption spectrometry (FAAS). Several parameters that govern extraction recovery, including extraction pressure, extraction temperature, extraction time, the density of $scCO_2$, and the amount of chelating agents spiked, are also investigated and optimized in this study. The accuracy of this proposed method is validated by the analysis of a commercial ITO etching reagent.

2. Experimental

2.1. Instrumentation

A schematic diagram of the experimental setup used in this study is mentioned elsewhere [18]. SFE were performed using an ISCO Model SFX 220 (ISCO, Inc., Lincoln, NE, USA) supercritical fluid extractor that was equipped with a linear coaxial restrictor heater and a 50 μm I.D. fused-silica capillary restrictor. An ISCO 260 D syringe pump delivered CO_2 to the extraction unit at a constant pressure. A 10 ml stainless steel extraction cartridge was used to load the samples into the extraction chamber. An extraction flow
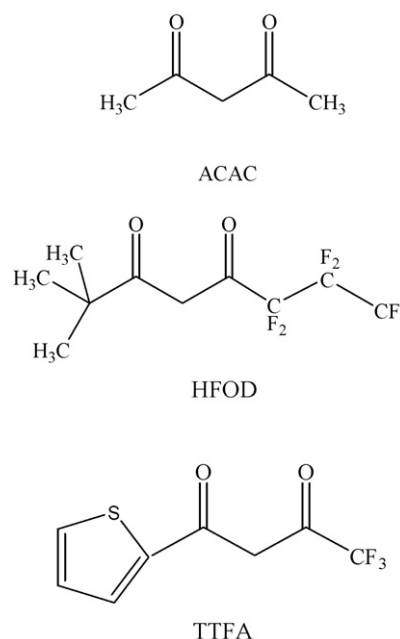

Fig. 1. Chemical structures and abbreviation for chelating agents used in $scCO_2$ extraction of indium from etching wastewater.

rate of approximately 1.0 ml min⁻¹ was regulated using a fused-silica capillary restrictor.

The indium (III) content in etching wastewater was determined by FAAS using a PerkinElmer Analyst AA200 equipped with an air/acetylene flame. The detection wavelength (nm) for indium was 303.94 nm with a spectral bandpass of 0.7 nm (low slit). A Mettler AG 245 microbalance (Mettler-Toledo, Inc., Switzerland) with 10 μg readability was used to weigh the reagents.

2.2. Reagents

The reagents used in this study included LC grade methanol, superpure grade HNO_3, and pro-analysis grade acetylacetone (ACAC) were purchased from Merck (Darmstadt, Germany). Thenoyltrifluoroacetone (TTFA) and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (HFOD) were of analytical reagent grade and obtained from Aldrich (Milwaukee, WI, USA). The chemical structures of these chelating agents are summarized in Fig. 1. The etching wastewater sample was obtained from a local AU Optronics (AUO) Corporation Facility. An In(III) atomic absorption stock solution (1000 ppm) was purchased from Merck (Darmstadt, Germany). Calibration standard solutions of In(III) were prepared by diluting In(III) standard stock solutions with 0.2% HNO_3. All glassware and polyethylene bottles were soaked in 10% HNO_3 for cleaning and then rinsed three times with de-ionized water. De-ionized water was produced using a Millipore Milli-Q apparatus (Milford, MA, USA) and used for all solutions and dilutions.

2.3. Procedures

2.3.1. Recovery of indium (III) from etching wastewater

Initially, the chelating agent and 3 ml of etching wastewater were loaded into the extraction cell. Liquid CO_2 was then delivered into the system and the chamber was pressurized using a high-pressure pump. The chamber pressure was controlled by a back-pressure regulator. After the system reached equilibrium (typically after about 5 min), the six-port valve was switched such that the $scCO_2$ was delivered to the cell. Five minutes of dissolution and saturation time was allowed for the $scCO_2$ to become saturated with

chelating agent, and the extraction time was calculated from this point.

The experiments were carried out in the pressure and temperature ranges of 17.2–24.1 MPa and 60–100 °C, respectively. The effects of different chelating agents, such as ACAC, TTFA and HFOD, on extraction recoveries were investigated. Extractions were performed with a 10 min static step, followed by a 10 min dynamic step. The restrictor was at ambient temperature. For each extraction, the extract was collected in a 30 ml trap that contained 5 ml of CH$_3$OH at ambient temperature.

2.3.2. Validation of the proposed method

In order to verify the accuracy of the proposed method, the recovery of In(III) from the single element standard solution was performed. The concentrations of the reference solutions were determined within 5% standard deviation. In this study, the limit of detection (LOD) of indium, as determined by FAAS, was 136.0 μg l^{-1}. The LOD was calculated as 3σ of the reagent blank. In order to determine the concentrations of In(III) in unknown samples, external calibration curves were constructed from serial dilutions of In(III) standard before each analytical run. Slopes (correlation coefficients of $r > 0.995$) for the external standard curves were computed and used to calculate the concentrations of unknown samples. Final concentrations were corrected with combined reagent and blanks. For each batch of samples, six samples were analyzed together using an auto sampler. Furthermore, the developed method was applied to the analysis of a commercial available ITO etching reagent (ITO-06SD) with satisfactory recovery, 91.8–105.6% ($n = 6$).

3. Results and discussion

3.1. Extraction recovery

The extraction behavior described in this work was evaluated as extraction recovery, which is defined as:

$$\text{extraction recovery}(\%) = \left(\frac{C_f}{C_i}\right) \times 100,$$

where C_i is the initial concentration of In(III) in the etching wastewater before extraction and C_f is the final concentration of In(III) remaining in the sample solution after extraction. Various parameters, including extraction temperature, extraction pressure, scCO$_2$ density and extraction time, were investigated to maximize the extraction recovery of In(III) ions from etching wastewater by scCO$_2$ extraction. In this study, SFE conditions were optimized using the step-by-step design developed by McNally [23]. This step-by-step approach is an alternative to the factorial design approach [24], as it generates similar results with relatively little data processing. In addition, all experiments are performed in static–dynamic mode, since static–dynamic extraction is more effective than static extraction and consumes less supercritical fluid. In this study, ACAC and two commercial fluorinated chelating agents (HFOD and TTFA) were evaluated.

3.2. Effect of extraction temperature

The effect of temperature on the extraction of In(III) from ITO etching wastewater was investigated at three different temperatures: 60, 80 and 100 °C. In the following experiments, the extraction pressure and extraction time were maintained at constant values of 17.2 MPa and 20 min, respectively. Three different chelating agents, ACAC, HFOD, and TTFA, were evaluated under the same extraction conditions. Among the chelating agents evaluated in this study, the extraction recovery of In(III) was the highest with HFOD as the chelating agent, whereas the recovery of In(III) was the lowest with ACAC as the chelating agent (Fig. 2). When
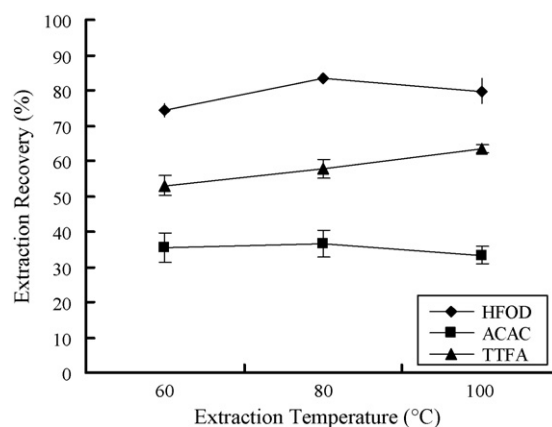
Fig. 2. Effect of temperature on extraction recovery of indium with three different chelating agents at 20.7 MPa and 20 min extraction time.

the extraction temperature was increased from 60 to 80 °C with the same extraction chelating agents, the peak extraction recovery was reached at 80 °C (Fig. 2). Increasing the temperature to 100 °C did not increase the recovery, since the high temperature increased chelating agent degradation and reduced extraction recovery. Therefore, 80 °C was found to be the optimal extraction temperature and was used for all subsequent scCO$_2$ extractions.

The effect of temperature on the extraction of indium with HFOD as a chelating agent was negligible since the extraction recovery remained constant at about 80.0% with increasing temperature. This result suggests that the formed In–HFOD complexes were highly stable and soluble at various different scCO$_2$ densities. On the other hand, in the case of ACAC, the extraction recovery remained constant at about 35.0% with increases in temperature from 80 to 100 °C. There are two plausible reasons for this low recovery. The first is that the formed indium (III) nitrate–ACAC complex may reach a certain solubility limit in the scCO$_2$ [16]. Another possibility is that the ACAC complex may be ineffective at attacking and liberating the indium from the ITO etching wastewater matrix.

3.3. Effect of extraction pressure

For an aqueous matrix, increasing the extraction pressure increases the cohesive energy of the supercritical fluid, which translates into reduced interaction of the fluid with the matrix because the surface area of the fluid is reduced [25]. The effect of pressure on the extraction recovery of indium is shown in Fig. 3. The three chelating agents were observed at pressures ranging from 17.2 to
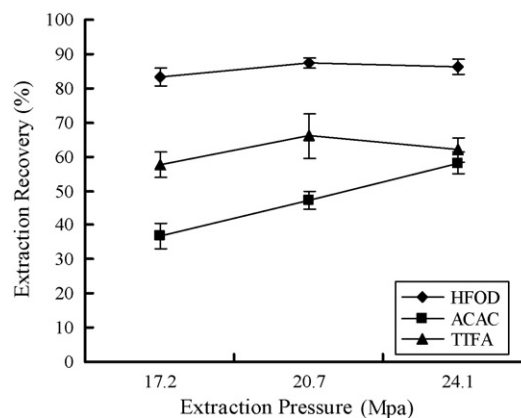
Fig. 3. Effect of pressure on extraction recovery of indium with three chelating agents at 80 °C and 20 min extraction time.
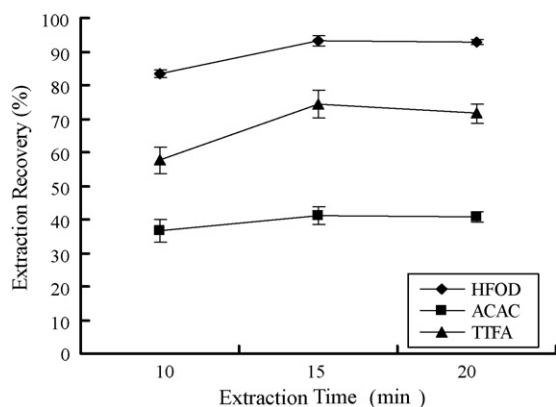
Fig. 4. Effect of extraction time on extraction recovery of indium with three chelating agents at 80 °C and 20.7 MPa.

24.1 MPa. The temperature and extraction time were maintained constant at 80 °C and 20 min, respectively. In the case of TTFA, the extraction recovery was low at 17.2 MPa and increased with increasing pressure up to 20.7 MPa; however, the recovery decreased when the pressure was further increased. Since the solubility of TTFA in scCO$_2$ may be higher at higher pressures, the lower recovery at 24.1 MPa may be due to decreased complex formation at a very high pressure. In the case of ACAC, extraction recovery gradually increased with pressure, suggesting that the solubilities of ACAC and ACAC–In complex in scCO$_2$ are higher at elevated pressures. In the case of HFOD, the extraction recovery reached its maximum of 87.3% at 20.7 MPa. Increasing the pressure of the system did not alter this recovery, and it remained constant under all of the investigated pressures. This result suggests that the In–HFOD complex was highly soluble in the scCO$_2$ in the evaluated range of scCO$_2$ densities.

3.4. Effect of extraction time

In previous experiments, the static and dynamic extraction times were both fixed at 10 min and the extraction recoveries were lower than 90.0%. Since extraction time is one of the major factors that determines the overall extraction recovery of metal from aqueous solutions by scCO$_2$, three static times (10, 15, and 20 min) were examined. The experiments were performed at a constant pressure and temperature of 20.7 MPa and 80 °C, respectively, and with a 10 min dynamic extraction time to improve extraction recovery. For these three chelating agents, 15 min static extraction was found to be the optimal static time for the extraction recovery of In(III) from waste etching solutions. Increasing the dynamic extraction time from 15 to 20 min did not improve extraction recovery. Therefore, the optimal static extraction time was set at 15 min in the following experiments. Moreover, the effect of three dynamic times (10, 15, and 20 min) after a 15 min static extraction time on the extraction of In(III) using scCO$_2$ at the optimized extraction pressure and temperature was investigated. As shown in Fig. 4, increasing the dynamic extraction time from 10 to 15 min improved the extraction recoveries for these three chelating agents; however, increasing the extraction time to 20 min did not improve the extraction recovery of In(III) from etching wastewater. Hence, the optimal extraction times were identified to be 15 min dynamic extraction and followed by 15 min static extraction in this study.

In this study, an extraction recovery of 93.3% could be achieved when using a 30 min total extraction time and HFOD as chelating agent. This suggests that HFOD forms a very stable and highly soluble metal complex with In(III). On the other hand, in the case of ACAC and TTFA, the extraction recoveries increased with time,

reaching maximums of around 41.2% and 74.7%, respectively, under the optimized extraction conditions. The extraction recovery for these two chelating agents did not increase after 40 min; although the chelating agents remained in the cell, the extraction did not proceed.

3.5. Effect of scCO$_2$ density

Since the solubility of any solute in scCO$_2$ is closely related to the density of the fluid, the pressure and temperature conditions used in Figs. 2 and 3 were used to calculate the density of scCO$_2$ which was re-plotted against the extraction recovery. In the case of HFOD and ACAC, the extraction recovery enhanced with increasing fluid density. Since the solubility of solute generally increases with the density of scCO$_2$, the solubility of the formed indium metal complex enhanced with increasing scCO$_2$ density, resulting in the increased extraction recovery shown in Fig. 5.

In the case of the TTFA chelating agent, the extraction recovery was not simply correlated with the fluid density. Temperature may have influenced extraction process by increasing the solvation power of the formed complex. At constant pressure, higher temperatures may lead to increased TTFA degradation, which would decrease the extraction recovery of In(III) by SFE [26]. With this chelating agent, In(III) was probably extracted in the form of an In(NO$_3$)$_2$(TTFA) complex [27].

3.6. Effect of the chelating agent

In general, the selection of suitable chelating agents for SFE is a critical step for in situ chelation with metal ions. In addition, the optimal molar ratios of chelating agent-to-In(III) were investigated at 3:1, 6:1, 8:1 and 10:1 in this study. The results indicate that the extraction recovery reaches a peak of 93.3% at an HFOD-to-In(III) ratio of 3:1. Beyond that ratio, recovery values remain steady. Due to the decomposition of the chelating agent in scCO$_2$, an excess amount of chelating agent was usually spiked in scCO$_2$ to increase metal extraction recovery [25]. Accordingly, the optimal molar ratio of chelating agents to In(III) ions was 6:1 for the scCO$_2$ extraction experiments.

In this study, SFE was performed at a pressure of 20.7 MPa at 80 °C during 15 min static and 15 min dynamic extractions using supercritical carbon dioxide in order to investigate the effect of different chelating agents on the extraction recovery of indium metal. Fig. 6 summarizes the effects of chelating agents on the extraction recovery of In(III) from ITO etching wastewater at 80 °C and different extraction pressures. In this study, the performance of chelating
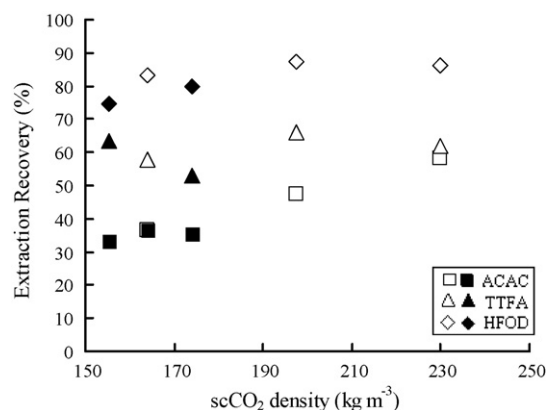

Fig. 5. Effect of scCO$_2$ density on the extraction recovery of indium (hollow symbols represent extraction at different temperatures and 20.7 MPa; solid symbols represent extraction at different pressures and at 80 °C).
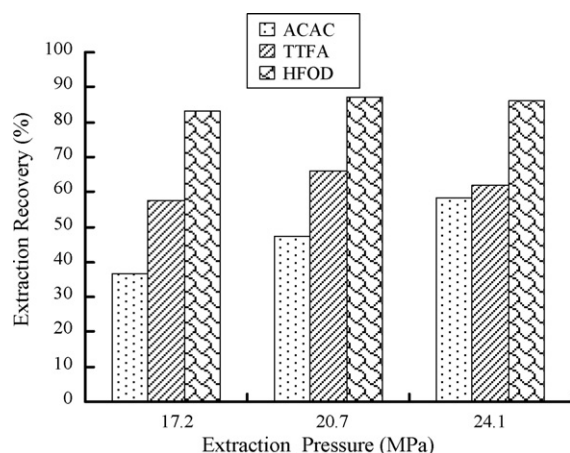
Fig. 6. Effect of chelating agent on the extraction recovery of indium at 80 °C and different extraction pressures.

agents in terms of the extraction recovery of In(III) ions followed the order of HFOD > TTFA > ACAC. Experimental results demonstrated that fluorinated chelating agents (e.g. HFOD, TTFA) were more effective than the non-fluorinated chelating agent (ACAC).

4. Conclusion

Based on the results of this study, indium metal was successfully extracted from real etching wastewater of ITO process by scCO$_2$ with a fluorinated β-diketone chelating agent. Three different chelating agents were investigated: ACAC, TTFA, and HFOD. Meanwhile, HFOD provided the maximum extraction recovery of 93.3% in a 30 min extraction at the optimal extraction pressure of 20.7 MPa and extraction temperature of 80 °C. On the other hand, ACAC and TTFA did not provide satisfactory extraction recoveries. This result suggests that ACAC and TFFA have decreased abilities to form complexes with indium.

Acknowledgements

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