

# Detection of Bromide Ions in Water Samples with a Nanomolar Detection Limit using a Potentiometric Ion-selective Electrode

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This paper presents a robust potentiometric solid-contact ion-selective electrode (ISE) for the rapid detection of bromide ions ( $\text{Br}^-$ ) in water samples. The sensing membrane contains poly (vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS) and ionophore without a lipophilic ion exchanger, and provides good potential responses for  $\text{Br}^-$  in the range of 0.010 to 1.0  $\mu\text{M}$ . The calibration curve demonstrates detection limits of  $2.0 \times 10^{-9}$  mol/L ( $3\sigma$ ) for bromide ions. Moreover, compared with previously reported  $\text{Br}^-$ -selective ISEs, the proposed ISE offers remarkably improved sensitivity for the detection of bromide and provides better selectivity coefficients for  $\text{HPO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ . The proposed sensor is successfully applied for the practical determination of  $\text{Br}^-$  in real water samples.

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**Keywords:** ISEs; Bromide ions; potentiometric; solid contact

## 1. INTRODUCTION

Bromide is naturally present in many treated and untreated water sources worldwide, particularly in ground water [1,2]. It is well known that chlorination or ozonation disinfection processes are commonly used to kill pathogen in drinking water source treatment [3,4,5]. However, these processes can generate a variety of chlorinated and brominated disinfection byproducts (DBPs) that are highly toxic for public human health at very low concentrations[6]. Among these DBPs derived from bromide as a precursor, bromate is classified as a potential human carcinogen by the International Agency for Research on Cancer [1,7]. Therefore, as the precursor of bromate, the concentration level of bromide in water sources has a significant impact on the quality of drinking

water. However, the low level of bromide in water source and drinking water makes it very challenging and requires the application of sensitive, fast and effective instrumental analysis.

Currently, a series of analytical methodologies have been developed for bromide detection in water samples. The most common methods involve inductively coupled plasma mass spectrometry (ICP-MS) [4,11] and ion chromatography (IC) using suppressed conductivity detection or amperometry and absorbance detectors [8,9,10]. Additionally, a number of attractive approaches involving capillary electrophoresis using direct UV detection [12,13], fluorescence spectrophotometry [2,14] and gas chromatography-mass spectrometry [7,15] have been reported for the detection of bromide. While these methods provide high recoveries and low detection limits, they require tedious pretreatment and the use of expensive instruments, and also lack reusability, resulting in a high cost per sample. The shortcomings of these classical analytical procedures can be potentially overcome using cost-effective, highly sensitive, and miniature electrochemical sensors. As highly successful electrochemical sensors, potentiometric ion-selective electrodes (ISEs), which allow simple, rapid and selective detection of analytes, have been used for the detection of relatively high concentrations of bromide from  $3.6 \times 10^{-6}$  M to  $1.6 \times 10^{-5}$  M [16,17,18,19]. Unfortunately, this poses serious limitations on their use for detecting the trace levels of bromide found in real water samples. As such, achieving lower detection limits for bromide is essential for the practical application of potentiometric ISEs to this end. However, systematic studies focused on the detection of trace levels of bromide in water by potentiometric ISEs are currently lacking.

The present study addresses this issue by exploring the use of solid contact ISEs with an ion-to-electron transducer layer between the ion-selective membrane (ISM) and the metal substrate. Thus, solid contact ISEs can eliminate the internal solution, and achieve a lower analyte detection limit [20]. Recently, similarly constructed ISEs have been successfully applied for detecting a number of organic and inorganic species at trace levels [21-25]. The present work extends this approach by developing sensitive and selective solid-contact Br<sup>-</sup>-ISEs. In particular, the influence of membrane components such as ionophores and ion exchangers are investigated, and the effect of conditioning protocols using either primary ions (Br<sup>-</sup>) or interfering ions (Cl<sup>-</sup>) is also studied. The experimental results demonstrate that the proposed solid-contact ISEs offer remarkably improved selectivity and sensitivity for the detection of bromide relative to conventional ISEs. The excellent analytical performance obtained herein suggests that this technology is promising for the design of in situ bromide sensing probes.

## 2. EXPERIMENTAL

### 2.1 Materials and reagents

High molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS), tridodecylmethylammonium chloride (TDMACl), poly(3-octylthiophene) (POT), meso-tetraphenylporphyrin manganese(III)-chloride complex (ionophore 1) and 4,5-Dimethyl-3,6-dioctyloxy-o-phenylene-bis(mercurytrifluoroacetate) (ionophore 2) were purchased from Sigma-Aldrich. All of the other chemicals were analytical-reagent grade. Tetrahydrofuran (THF) was freshly distilled prior to use. All of the other reagents obtained from Sinopharm Chemical Reagent Co., Ltd

(Shanghai, China), were analytical grade and used as received. Aqueous solutions were prepared by dissolving the appropriate salts in the freshly de-ionized water with a specific resistance of 18.2 M $\Omega$  cm obtained using a Pall Cascada laboratory water system.

## 2.2 Preparation of solid-contact Br<sup>-</sup>-ISE

The following bromide-selective membranes were prepared by dissolving 250 mg of the stated components in 2.0 mL of THF.

Membrane I: PVC (33 wt%), DOS (66 wt%), and ionophore 1 (1 wt%).

Membrane II: PVC (33 wt%), DOS (66 wt%), and ionophore 2 (1 wt%).

Membrane III: PVC (33 wt%), DOS (65 wt%), ionophore 2 (1 wt%), and TDMACl (1 wt%).

Each membrane cocktail was degassed by sonication for 10 min before use. The glass carbon electrodes were carefully polished using 500 nm alumina nanoparticles suspensions on a felt pad for about 10 min, thoroughly cleaned in an ultrasonic cleaner with water, bathed for 5 min in acetone, and allowed to dry completely in air. The cleaned electrodes were then introduced into a fitting PVC tube at a depth of 1 mm. A layer of the conductive polymer POT was deposited on the electrode surface by drop-casting 50  $\mu$ L of a 25 mM chloroform solution, and the solvent left to evaporate for at least 5 min. Subsequently, 100  $\mu$ L of a membrane cocktail was drop cast on the top of the POT layer, and then left to dry at room temperature. Before use, the electrodes were conditioned in either a 10<sup>-4</sup> M NaCl solution for 1 d or in a 10<sup>-4</sup> M NaBr solution for 1 d.

## 2.3 EMF measurements

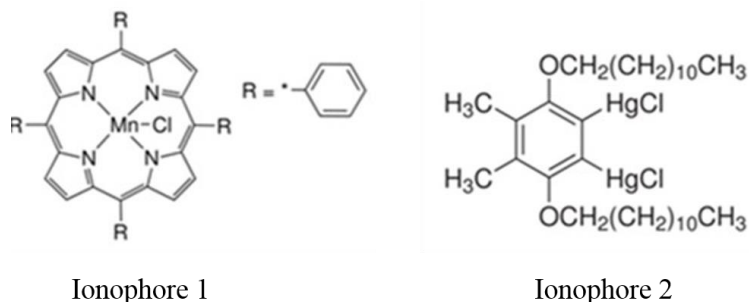
All electromotive force measurements (EMF) were carried out at 25 °C using a CHI 760D electrochemical workstation (Shanghai, China) in the following galvanic cell: SCE/1 M LiOAC/sample solution/Br<sup>-</sup>-sensing membrane/POT/glass carbon. The EMF values were corrected for liquid junction potentials using the Henderson equation, and ion activities were calculated according to the Debye-Hückel approximation. The selectivities of the Br<sup>-</sup>-ISE were examined by the separated solutions method [26].

# 3. RESULTS AND DISCUSSION

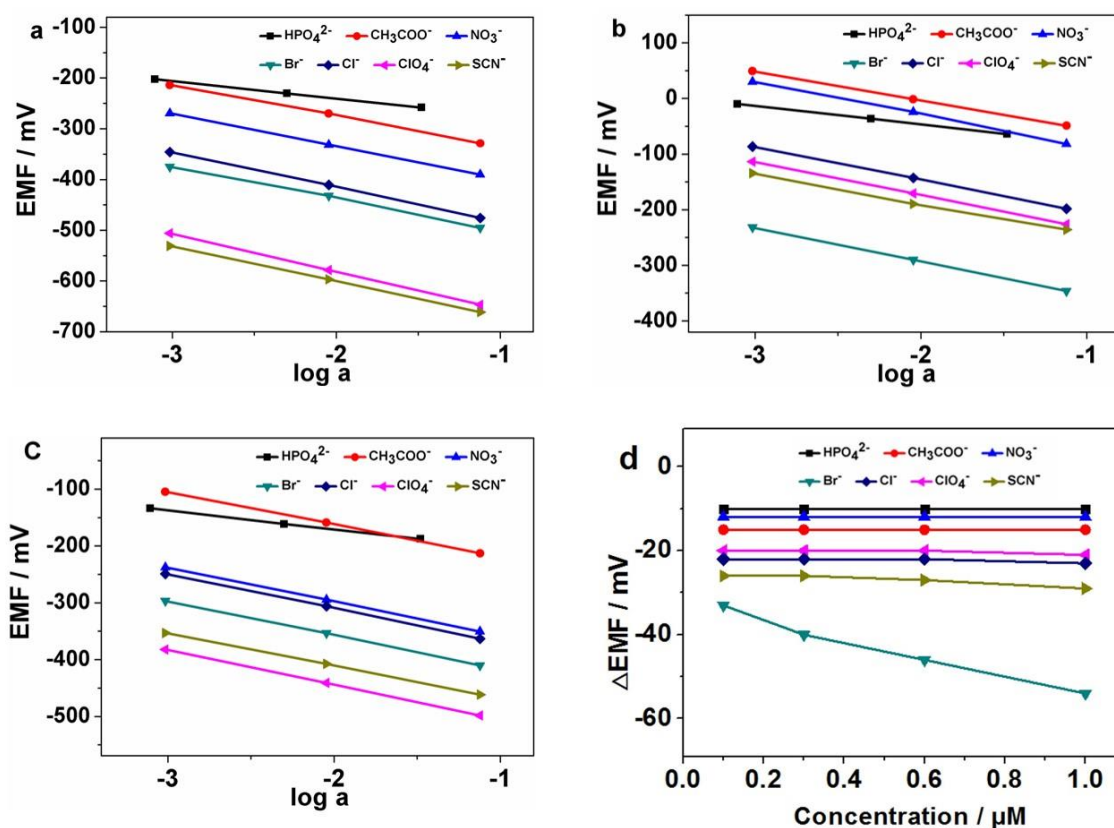
## 3.1. Fabrication of solid-contact bromide-selective electrode

It is well established that membrane composition, especially the ionophore, plays an important role in potentiometric sensor performance. The chemical structure of the ionophore has a significant effect on the selectivity of the electrodes [27]. This work employs a metalloporphyrin compound denoted herein as ionophore 1, and a type of mercury organic compound denoted as ionophore 2. These compounds are illustrated in Figure 1. A previous study demonstrated that a charged carrier mechanism is conceivable for ionophore 1, while electrodiffusion transport experiments have

demonstrated that ionophore 2 provides a response mechanism based on a neutral carrier [30]. Thus, we first evaluated the potentiometric responses of the electrodes employing membranes I, II, and III based on ionophores 1 and 2 for the sodium salts of the anions  $\text{HPO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ , and  $\text{SCN}^-$ .



**Figure 1.** The chemical structure of the ionophores.



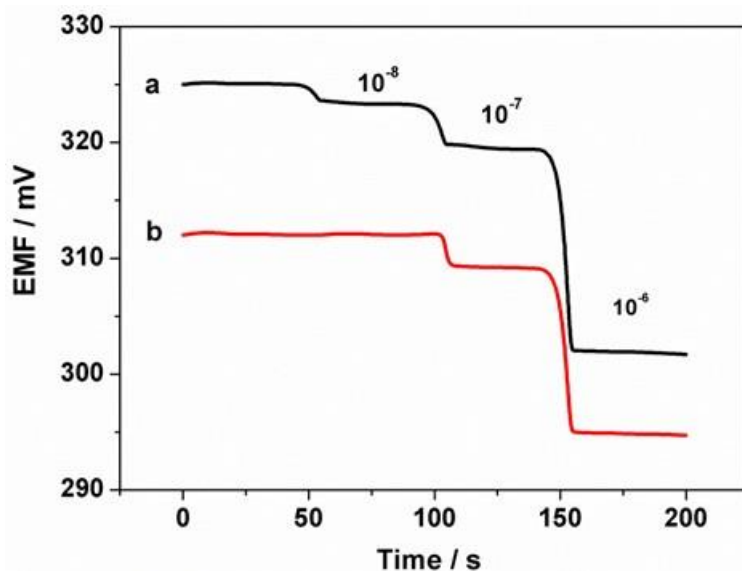
**Figure 2.** Potential responses of the bromide selective electrode toward the sodium salts of the anions ( $\blacksquare$ )  $\text{HPO}_4^{2-}$ , ( $\bullet$ )  $\text{CH}_3\text{COO}^-$ , ( $\blacktriangle$ )  $\text{NO}_3^-$ , ( $\blacktriangledown$ )  $\text{Br}^-$ , ( $\blacklozenge$ )  $\text{Cl}^-$ , ( $\blacktriangleleft$ )  $\text{ClO}_4^-$  and ( $\blacktriangleright$ )  $\text{SCN}^-$ . The membranes composition are as follows: (a) 33 wt% PVC, 66 wt% DOS and 1 wt% ionophore 1; (b and d) 33 wt% PVC, 66 wt% DOS and 1 wt% ionophore 2; (c) 33 wt% PVC, 65 wt% DOS, 1 wt% ionophore 2 and 1 % wt% TDMACl.

These results are presented in Figure 2. Here, membranes I and II differ only in terms of the ionophore employed, and therefore the results in Figures 2(a) and (b) represent a good basis for

comparison. As can be seen from Figure 2(a), the electrode employing membrane I doped with ionophore 1 exhibits better selectivity for  $\text{CH}_3\text{COO}^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{NO}_3^-$ , and no selectivity for  $\text{ClO}_4^-$  and  $\text{SCN}^-$ , which have strong lipophilicity. Moreover, the electrode provides unsatisfactory selectivity for  $\text{Cl}^-$ , which is the primary ion interfering with the detection of bromide in water. However, as shown in Figure 2(b), the replacement of ionophore 1 with ionophore 2 yields a significantly improved selectivity for interfering ions, particularly for  $\text{Cl}^-$ . Therefore, ionophore 2 (i.e., membranes II and III) was selected for further study.

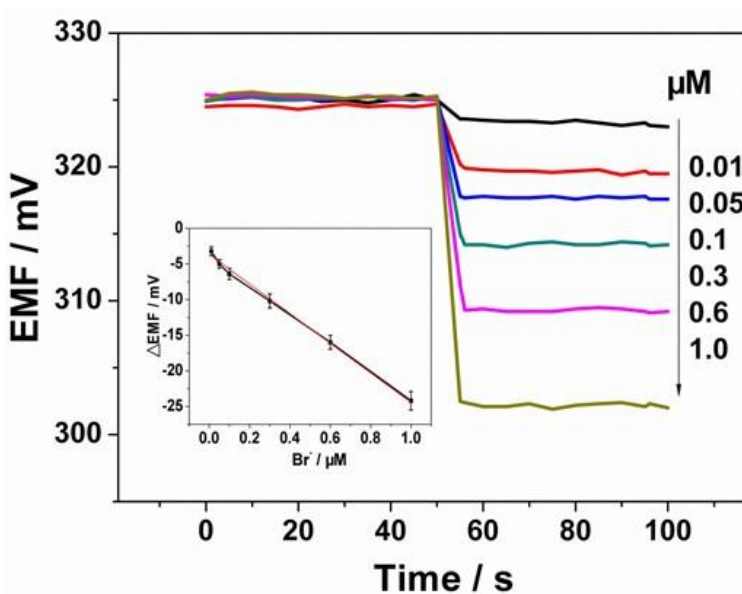
Conventional potentiometric ISEs are based on hydrophobic plasticized polymeric membranes or films that are doped with a lipophilic ion exchanger, which is responsible for extracting the analyte ions from the sample and transporting them to the membrane [28,29,30]. Moreover, it has been found that the presence of a lipophilic anion exchanger in the sensing membrane drastically reduces the degree of interference encountered from lipophilic anions in samples. However, some ISE, sensors based on an ionophore and without a lipophilic ion exchanger such as TDMACl demonstrated the expected selectivity for other interfering anions [31]. For example, chloride-selective polymeric membranes without a lipophilic ion exchanger have demonstrated better selectivity for other common anions [31]. Therefore, the present work also studied the effect of the ion exchanger on the selectivity of the proposed potentiometric bromide-selective electrodes. Here, membranes II and III differ only in terms of the ion exchanger employed, and therefore the results in Figures 2(b) and (c) represent a good basis for comparison. It was shown in Figure 2(c) that the bromide-selective electrode with TDMACl exhibits no selectivity for  $\text{ClO}_4^-$  and  $\text{SCN}^-$ , and poorer selectivity for other anions such as  $\text{CH}_3\text{COO}^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{NO}_3^-$  than that of the ISE fabricated without TDMACl, as shown in Figure 2(b). This is probably because the mercury organic compound behaves as an electrically neutral ionophore in the membrane phase, and forms negatively charged complexes with the analyte anions [31]. The membrane electrode doped with TDMACl as an anion exchanger more effectively extracts interfering anions, and therefore has poorer selectivity. As shown in Figure 2(d) for the ISE employing membrane II, negligible potential changes are observed for interfering anions in the concentration range of  $10^{-7}$ – $10^{-6}$  M. These results indicate that the membrane II ISE based on a mercury organic compound as an ionophore and without an anion exchanger offers promising potential use for low-level  $\text{Br}^-$  bromide ion detection. Therefore, the fabricated electrodes uniformly employed membrane II in subsequent testing.

The effect of the conditioning protocols using primary ions and interfering ions on potential response is shown in Figure 3. It can be clearly seen that the electrode conditioned in  $10^{-4}$  M NaBr has almost no potential response for  $\text{Br}^-$  ions at  $10^{-8}$  M. However, conditioning the electrode using interfering  $\text{Cl}^-$  ions it provides a potential response of 3–5 mV for  $\text{Br}^-$  ions at  $10^{-8}$  M. This is mainly because the chloride ions in the membrane were replaced by bromide ions with higher lipophilicity. Therefore, the fabricated electrodes were conditioned in NaCl at a concentration of  $10^{-4}$  mol/L for 1 d in subsequent testing.



**Figure 3.** Potential response of the bromide-selective electrode employing membrane II at various Br<sup>-</sup> molar concentrations (a: conditioned in 10<sup>-4</sup> mol/L NaCl for 1 d; b: conditioned in 10<sup>-4</sup> mol/L NaBr for 1 d).

3.2. Potential response behavior, limit of detection, and selectivity of the bromide-selective electrode



**Figure 4.** Potential response of the proposed bromide anion ISE. The resulting calibration curve for the detection of bromide is given in the inset.

The limit of detection (LOD) of the proposed Br<sup>-</sup>-ISE was evaluated using three identically prepared Br<sup>-</sup>-ISEs. Figure 4 shows the potential traces of the respective ISEs over a bromide ion concentration range of 0.01 to 1.0 μM, and the corresponding calibration curve is given in the inset. It can be seen from the inset of Figure 4 that the potential response is proportional to the concentration of bromide ions over the entire range considered. The calibration curve indicated an LOD of  $2.0 \times 10^{-9}$

mol/L ( $3\sigma$ ) for bromide ions. In addition, the performance of the proposed sensor was compared with those of previously reported bromide membrane electrodes, and the results are listed in Table 1. As shown in the table, the proposed Br<sup>-</sup>-ISE in this work provides a superior LOD, even though the reported sensors offer wider Br<sup>-</sup> concentration ranges. Thus, the proposed Br<sup>-</sup>-ISE can be applied to water samples with low bromine ion contents.

**Table 1** Comparison of the performance of the proposed Br<sup>-</sup>-ISEs with the reported electrodes

Ref. no.	Calibration Range (M)	Detection Limit (M)
[5]	$3.2 \times 10^{-5}$ to $1.0 \times 10^{-1}$	$2.0 \times 10^{-5}$
[16]	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$	$3.6 \times 10^{-6}$
[17]	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	$1.6 \times 10^{-5}$
[19]	$2.2 \times 10^{-6}$ to $1.0 \times 10^{-1}$	$1.4 \times 10^{-6}$
This work	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-6}$	$2.0 \times 10^{-9}$

The selectivity coefficients of the bromide-ISE over the most important interfering anions were calculated by the separate solution methods (SSM) and summarized in Table 2. Beyond the poor selectivity coefficients over perchlorate and thiocyanate, the potentiometric log selectivity coefficients were  $-5.3$ ,  $-4.9$ ,  $-2.5$  and  $-4.9$  for HPO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> respectively. This selectivity satisfied the requirements for bromide determination in water samples.

**Table 2.** Potentiometric selectivity coefficients for the bromide-selective electrode

Ion J	$\log K_{I,J}^{pot}$	Ion J	$\log K_{I,J}^{pot}$
HPO <sub>4</sub> <sup>2-</sup>	$-5.3 \pm 0.1$	ClO <sub>4</sub> <sup>-</sup>	$-2.0 \pm 0.1$
CH <sub>3</sub> COO <sup>-</sup>	$-4.9 \pm 0.3$	SCN <sup>-</sup>	$-1.7 \pm 0.2$
NO <sub>3</sub> <sup>-</sup>	$-4.9 \pm 0.2$	Cl <sup>-</sup>	$-2.5 \pm 0.2$

### 3.3. Real sample analysis

To evaluate the feasibility of the proposed sensor, the Br<sup>-</sup> contents in real water samples from a local public water source and lake water were determined using the standard addition method. To avoid any effect of Cl<sub>2</sub> on the accuracy of the detection results, all of the water samples were first boiled to remove this component. For comparison, the water samples were also tested using the Ion Chromatography (IC) method. The results are listed in Table 3. As can be seen, Br<sup>-</sup> was not detected in tap water, but it was detected in lake water samples with recoveries of 87%. Moreover, the data obtained using the proposed Br<sup>-</sup>-ISE agree well with the data obtained by the IC method. These results suggest that the proposed sensor is a promising and reliable tool for the detection of Br<sup>-</sup>.

**Table 3.** Application of the proposed sensor to determination of Br<sup>-</sup> in real samples

Sample	Proposed sensor ( $\mu\text{M}$ ) <sup>a</sup>	Recovery results			IC ( $\mu\text{M}$ ) <sup>a</sup>
		Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ ) <sup>a</sup>	Recovery (%)	
Tap water	N.D	0.50	0.45 $\pm$ 0.06	90	N.D
Lake water	0.46 $\pm$ 0.05	0.50	0.90 $\pm$ 0.05	87	0.42 $\pm$ 0.04

<sup>a</sup> Average of three measurements  $\pm$  standard deviation

#### 4. CONCLUSIONS

In summary, we have demonstrated a sensitive and selective solid-contact ISE for the detection of bromide ions in water. The proposed Br<sup>-</sup>-ISE without TDMACl in the membrane provided better selectivity coefficients for HPO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. The proposed solid-contact ISE was demonstrated to offer remarkably improved sensitivity for the detection of bromide ions relative to conventional ISEs. The results suggest that the proposed sensor is a promising and reliable alternative for the detection of bromide ions in water samples.

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