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# Direct Determination of Inorganic Mercury in Ethanol Fuel by Cold Vapor Atomic Absorption Spectrometry

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**ABSTRACT:** A simple method for the direct determination of mercury in ethanol fuel samples diluted with water by cold vapor atomic absorption spectrometry (CV-AAS) is proposed. The chemical parameters (concentrations of  $\text{NaBH}_4$  and  $\text{HCl}$ ) used for the Hg vapor generation for its measurement by CV-AAS were optimized. The calibration curve showed a linear response over the studied range ( $1\text{--}25\ \mu\text{g L}^{-1}$ ), with a correlation coefficient of 0.9999 and limits of detection and quantification of 0.05 and  $0.17\ \mu\text{g L}^{-1}$ , respectively. The relative standard deviations were lower than 3.5%. The accuracy of the method was estimated by applying the recovery test, and recovery values obtained were 84 and 106%. A sample throughput of  $45\ \text{h}^{-1}$  was achieved. Simplicity and sensitivity are among the advantages offered by the proposed method.

## 1. INTRODUCTION

The use of biofuels as a renewable energy source is considered one of the alternatives available to reduce air pollution and global warming.<sup>1</sup> The most commonly used renewable fuel is bioethanol, which can be produced from various types of plants. Ethanol fuel is obtained in Brazil from the fermentation of sugar cane, and this process is now very well established. According to the Renewables 2011 Global Status Report,<sup>2</sup> Brazil is the world's second largest producer of ethanol, corresponding to almost 37% of the production worldwide.

Although less polluting than fuels derived from petroleum, knowledge of the types of organic and inorganic contaminants present in ethanol fuel is essential, because some of these species are harmful to human health and the environment when emitted as pollutants in the combustion process. One of the parameters employed to evaluate the quality of ethanol fuel is the level of contamination by metallic ions, which may occur during the production process, transportation, and storage.<sup>3</sup> The presence of trace metal ions, such as mercury, in ethanol fuel is important in terms of engine maintenance, because metallic species can accelerate the corrosion of engines or promote the formation of gums and sediments. Also, the release of toxic elements during ethanol fuel combustion is a source of atmospheric pollution.<sup>4</sup>

In Brazil, the National Agency of Petroleum, Natural Gas and Biofuels (ANP) establishes quality standards for only a few chemical species in ethanol fuel, and mercury is not among them.<sup>5</sup>

It is well-known that mercury is a pervasive, highly toxic contaminant and is readily accumulated by organisms. Mercury is distributed throughout the environment, originating from both natural sources (e.g., volcanic eruptions and weathering of rocks) and human activities (e.g., battery production and agriculture and metallurgical processes).<sup>6</sup> The most likely route for the contamination of ethanol fuel by mercury is the incorporation of this metal during sugar cane growth, because of the intensive use of fertilizers,<sup>7</sup> vinasse,<sup>8</sup> and sewage sludge<sup>8,9</sup> to increase the cane productivity.<sup>10</sup>

Mercury is a difficult element to measure in complex matrices because the matrix must be destroyed at an elevated temperature without the loss of the analyte or contamination. Therefore, the determination of Hg in gasoline and other fuels derived from petroleum is hindered by the volatile nature of both mercury and the matrix, which may lead to considerable losses. The difficulty associated with the conversion of this kind of sample in aqueous solution represents a challenge in mercury determination.

Some studies based on cold vapor inductively coupled plasma mass spectrometry (CV-ICP-MS),<sup>11</sup> gas chromatography with inductively coupled plasma mass spectrometry (GC-ICP-MS),<sup>12</sup> electrothermal atomic absorption spectrometry (ET-AAS),<sup>13</sup> cold vapor fluorescence atomic spectroscopy (CV-AFS),<sup>14</sup> and cold vapor atomic absorption spectrometry (CV-AAS)<sup>15</sup> have been reported for the determination of mercury in fuels; however, procedures used, including sample pretreatment and preconcentration steps, have to be followed to ensure sensitivity, accuracy, and reproducibility.

Nowadays, the most employed method for Hg determination in different matrices, such as biological tissues,<sup>16</sup> water,<sup>17</sup> sediments,<sup>18</sup> blood,<sup>19</sup> and foods,<sup>20</sup> is CV-AAS, because it is a very sensitive and relatively low cost.<sup>20,21</sup> This technique is based on the chemical reduction of mercury to elemental Hg, followed by measurement of mercury vapor absorption at 253.7 nm.<sup>18,20</sup>

The aim of this work is the development of a method for the direct determination of  $\text{Hg}^{\text{II}}$  in ethanol fuel samples by CV-AAS without further sample pretreatment.

## 2. EXPERIMENTAL SECTION

**2.1. Instrumentation.** For mercury determination, a Varian (Victoria, Australia) SpectrAA-220 flame atomic absorption spectrophotometer equipped with a continuous flow Varian VGA 77 vapor generation accessory was used. The VGA system consists of a three-

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channel peristaltic pump equipped with Tygon and polyethylene tubes that carry the sample through a reaction coil, where it is acidified and mixed with a suitable reductant. The mercury vapor formed is transferred to an absorption cell for determination by the spectrometer.<sup>22</sup> The mercury hollow cathode lamp (Varian) was operated at 4.0 mA; the wavelength was set to 253.7 nm; and the spectral bandpass was set to 0.5 nm. The sample, HCl, NaBH<sub>4</sub>, and nitrogen gas were introduced at flow rates of 7, 1, 1, and 100 mL min<sup>-1</sup>, respectively. These instrumental parameters of VGA 77 were set as recommended by the manufacturer. The reaction time obtained after optimization was 60 s.

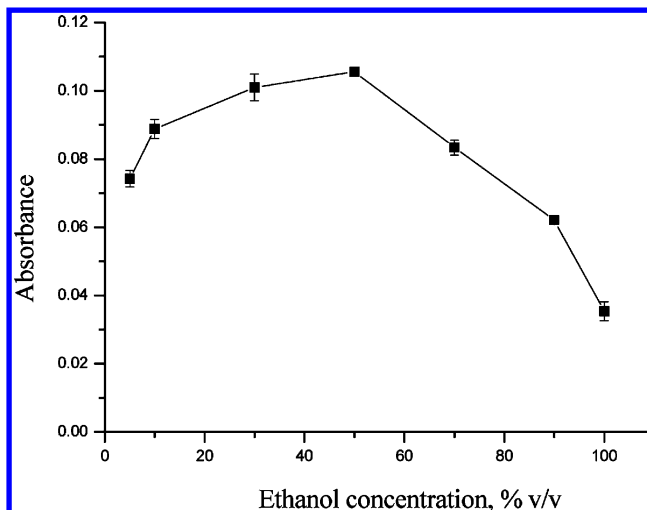
**2.2. Reagents, Solutions, and Samples.** All chemical reagents were of analytical grade. The water was deionized in a Milli-Q system (Gehaka, São Paulo, Brazil). Working standard solutions of Hg<sup>II</sup> were prepared by appropriate dilution of a 1000 mg L<sup>-1</sup> Hg<sup>II</sup> stock standard solution (Merck, Darmstadt, Germany) in ethanol medium. The NaBH<sub>4</sub> (Merck) solutions were prepared in the range of 0.1–0.6% (w/v) in 0.5% (w/v) NaOH (Vetec, Rio de Janeiro, Brazil). Solutions of HCl were obtained by appropriate dilution of concentrated HCl of 36.5–38.0% purity (Vetec). Nitrogen with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the carrier gas. Ethanol of 95% purity was purchased from Vetec. Ethanol fuel samples were obtained from local vendors and were prepared simply by obtaining a 2-fold dilution of the solution in water. The calibration solutions employed in the sample analysis were prepared in 50% (v/v) ethanol.

### 3. RESULTS AND DISCUSSION

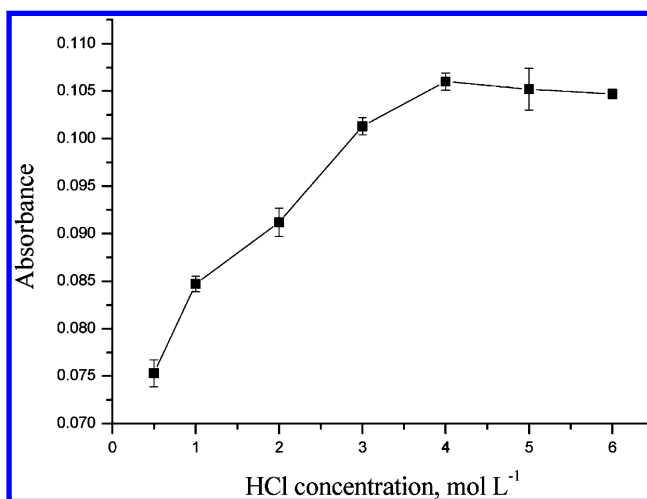
**3.1. Optimization of the Working Conditions.** Studies were carried out to evaluate the effect of varying the percentage of ethanol and the concentration of HCl as the carrier solution and NaBH<sub>4</sub> as the reducing agent in the cold vapor generation of mercury from ethanol solutions.

An ethanol–water mixture is known to exhibit anomalous physical–chemical properties.<sup>23</sup> When ethanol is added to water, some hydrogen bonds are broken, with new hydrogen bonds between water and alcohol being formed,<sup>24,25</sup> which induces a surface excess of the alcohol.<sup>26</sup> As a consequence, the viscosity of the ethanol–water mixture shows a nonlinear dependence<sup>27</sup> and surface tension is lowered because of the addition of ethanol.<sup>28</sup> These properties can play an important role in the kinetics of the mercury vapor release from the ethanol solution. Thus, the effect of varying the percentage of ethanol in Hg<sup>II</sup> aqueous solutions was studied in the range of 5–100% (v/v), using fixed concentrations of 10 µg L<sup>-1</sup> Hg<sup>II</sup>, 0.4% (w/v) NaBH<sub>4</sub> in 0.5% (w/v) NaOH, and 4 mol L<sup>-1</sup> HCl. It was verified that the absorbance increased gradually with an increasing percentage of ethanol up to 50% (v/v) (Figure 1), over which a decrease in the signal was observed. The decrease of absorbance may be attributed to aggregation of ethanol molecules at the surface and bulk solution (ethanol concentration higher than 50%, v/v),<sup>27,29,30</sup> which affect the partition equilibrium of reduced mercury between the aqueous and gas phases.<sup>31,32</sup> Koirtiyohann and Khalil reported that the reduced mercury follows a well-behaved partition function when equilibrated between a gas and an aqueous phase.<sup>32</sup> The optimum conditions for the vapor generation were maintained simply by preparing ethanol fuel samples in a 2-fold dilution in water.

The effect of the HCl concentration on the Hg<sup>II</sup> signal was examined in the range of 0.5–6 mol L<sup>-1</sup>, using fixed concentrations of 10 µg L<sup>-1</sup> Hg<sup>II</sup> in 50% (v/v) ethanol solution and 0.4% (w/v) NaBH<sub>4</sub> in 0.5% (w/v) NaOH. The results are shown in Figure 2. The maximum absorbance was observed when 4 mol L<sup>-1</sup> HCl was used, and at higher HCl concentrations, the Hg<sup>II</sup> intensity signal remained almost



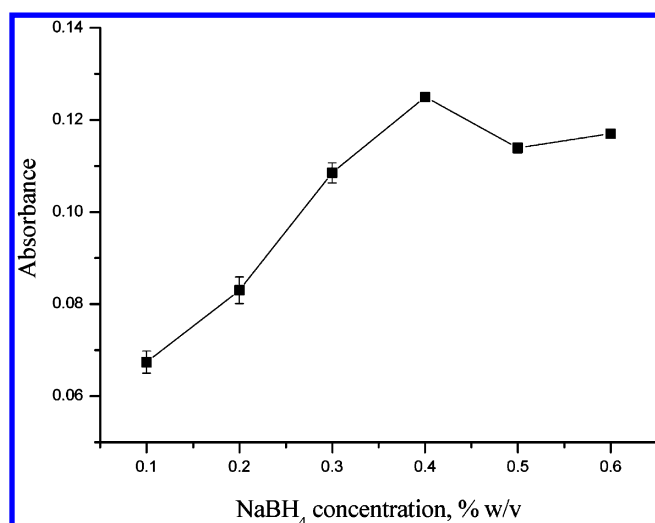
**Figure 1.** Effect of the ethanol percentage on the 10 µg L<sup>-1</sup> Hg<sup>II</sup> signal. Experimental conditions: 0.4% (w/v) NaBH<sub>4</sub> in 0.5% (w/v) NaOH and 4 mol L<sup>-1</sup> HCl.



**Figure 2.** Effect of the HCl concentration on the 10 µg L<sup>-1</sup> Hg<sup>II</sup> signal. Experimental conditions: 0.4% (w/v) NaBH<sub>4</sub> in 0.5% (w/v) NaOH and 50% (v/v) ethanol solution.

constant. Thus, 4 mol L<sup>-1</sup> HCl was selected for further experiments.

The efficiency of SnCl<sub>2</sub> as a reducing agent for the cold vapor generation of mercury was tested. However, the absorbance values obtained with SnCl<sub>2</sub> were much lower when compared to those obtained using NaBH<sub>4</sub>. More concentrated SnCl<sub>2</sub> solutions were not tested to avoid memory effects. NaBH<sub>4</sub> is known as an important and efficiency reducing agent, and good accuracy and sensitivity have been obtained in several studies using it for mercury reduction.<sup>18,20,33,34</sup> According to exposed and better repeatability obtained, NaBH<sub>4</sub> was chosen for all further determinations. The effect of the NaBH<sub>4</sub> concentration on the Hg<sup>II</sup> signal in the range of 0.1–0.6% (w/v) was examined, using fixed concentrations of 10 µg L<sup>-1</sup> Hg<sup>II</sup> and 4 mol L<sup>-1</sup> HCl. As shown in Figure 3, the Hg absorbance increased with the increase in the concentration of NaBH<sub>4</sub> up to 0.4% (w/v) and then decreased at higher concentrations. The decrease in the signal for higher concentrations of reducing agent can be related to dilution of the mercury vapor by the excess of hydrogen gas produced.<sup>35,36</sup> The NaBH<sub>4</sub> concen-



**Figure 3.** Effect of the NaBH<sub>4</sub> concentration on the 10 µg L<sup>-1</sup> Hg<sup>II</sup> signal. Experimental conditions: 4 mol L<sup>-1</sup> HCl and 50% (v/v) ethanol solution.

tration selected for the subsequent experiments was 0.4% (w/v) in 0.5% (w/v) NaOH.

**3.2. Interference Studies.** The interference studies were carried out by evaluating the interference effects of Cd<sup>II</sup>, Cu<sup>II</sup>, Fe<sup>III</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup>. These are representative interfering metal species present in ethanol fuel samples.<sup>37–39</sup> The tolerance limits of interfering species are established at the concentration required to cause no more than a ±10% error in the recovery of Hg<sup>II</sup> at 3 µg L<sup>-1</sup>.<sup>40,41</sup>

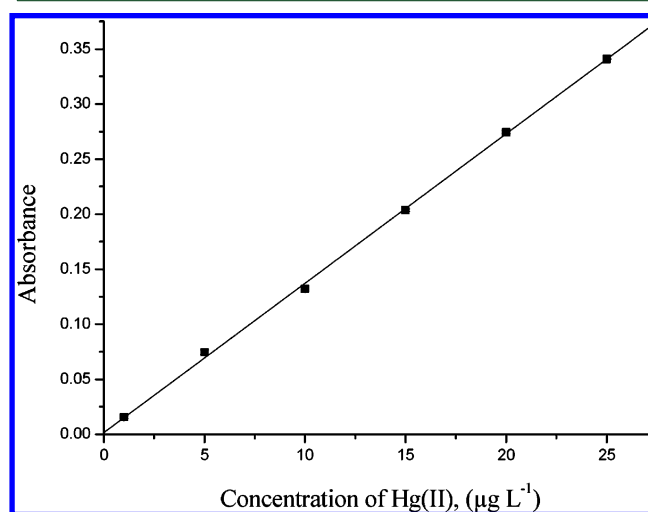
The interference studies were performed using an interferent/Hg<sup>II</sup> ratio of 1:1, 6:1, 10:1, and 20:1. In the experiment, 0.4% (w/v) NaBH<sub>4</sub> and 4 mol L<sup>-1</sup> HCl were used. It was found that Cd<sup>II</sup>, Ni<sup>II</sup>, and Pb<sup>II</sup> showed significant interference in the Hg<sup>II</sup> determination. No interferences of Cu<sup>II</sup> and Fe<sup>III</sup> were observed. The results can be seen in Table 1. The presence of metal ions causes serious interference in the signal during mercury determination by CV-AAS in either the liquid phase or gaseous phase. The interfering ions in the liquid phase can compete with the analyte for the reaction with sodium tetrahydroborate and precipitate in the form of metal borohydride species.<sup>42</sup> In the gaseous phase, the interferents can be simultaneously reduced to volatile species and, thus, influence the reduction of mercury into its elemental form.<sup>43,44</sup>

To minimize the effect of interfering ions, the effect of the HCl concentration (4–6 mol L<sup>-1</sup>) was measured, applying the same interferent/Hg<sup>II</sup> ratio studied previously. It was observed that the effects of interfering ions have been eliminated using 5 mol L<sup>-1</sup> HCl. According to Welz et al.,<sup>45</sup> an increase in the hydrochloric acid concentration improves the range of interference-free hydride-forming elements. The increase in the HCl concentration probably prevents the reduction of interfering ions and their interaction with the mercury vapor.

**3.3. Analytical Figures of Merit and Application.** The calibration curve using Hg<sup>II</sup> standard solutions was linear in the concentration range of 1–25 µg L<sup>-1</sup>. The linear regression equation was  $y = 0.00149 + 0.0136x$ , with a correlation coefficient of 0.9999. The calibration curve for mercury at the optimum conditions is shown in Figure 4. The limit of detection (LOD) and the limit of quantification (LOQ) based on  $3r/s$  and  $10r/s$ , where  $r$  is the standard deviation of 10 measurements of the blank and  $s$  is the slope of the calibration

**Table 1.** Interference Effect of Some Ions in the Recovery of 3 µg L<sup>-1</sup> Hg<sup>II</sup> in 50% (v/v) Ethanol Solution Using the Proposed Method

interferent	interferent/Hg <sup>II</sup>	recovery (%)
Cd <sup>II</sup>	1:1	116 ± 0.6
	6:1	114 ± 0.8
	10:1	103 ± 0.6
	20:1	91 ± 0.2
Cu <sup>II</sup>	1:1	101 ± 1.3
	6:1	102 ± 0.5
	10:1	106 ± 2.7
	20:1	104 ± 0.3
Fe <sup>III</sup>	1:1	106 ± 3.9
	6:1	110 ± 5.6
	10:1	97 ± 0.9
	20:1	94 ± 4.8
Ni <sup>II</sup>	1:1	105 ± 1.2
	6:1	111 ± 1.1
	10:1	97 ± 6.3
	20:1	108 ± 1.9
Pb <sup>II</sup>	1:1	111 ± 5.4
	6:1	113 ± 0.7
	10:1	114 ± 1.6
	20:1	104 ± 4.2



**Figure 4.** Calibration curve for mercury. Experimental conditions: 0.4% (w/v) NaBH<sub>4</sub> in 0.5% (w/v) NaOH, 4 mol L<sup>-1</sup> HCl, and 50% (v/v) ethanol solution.

graphs,<sup>46</sup> were 0.05 and 0.17 µg L<sup>-1</sup>, respectively. As shown in Table 2, the LOD of the proposed method is comparable to those obtained by da Silva et al. for the determination of mercury in ethanol by photo-CV-AAS<sup>47</sup> and better than those reported in the literature that determined mercury in gasoline by CV-ICP-MS,<sup>11</sup> natural gas condensates by GC-ICP-MS,<sup>12</sup> petroleum by ET-AAS,<sup>13</sup> and gasoline by CV-AAS<sup>15</sup> and CV-GF-AAS.<sup>36</sup> Some of these methods do not offer sufficient sensitivity for the direct determination, and a pre-concentration step is required. Other methods could be more attractive because of their lower detection limits, but they employ more expensive techniques. The method developed in this study does not require any harsh or time-consuming sample pretreatment and is, thus, suitable for the determination of mercury in ethanol fuel samples. The sample throughput of the method is 45 h<sup>-1</sup>.

**Table 2. Comparison of Methods for Hg<sup>II</sup> Determination in Petroleum Products**

sample	LOD ( $\mu\text{g L}^{-1}$ )	detection technique <sup>a</sup>	analytical strategy	reference
gasoline, diesel, biodiesel, and engine oil	0.20	CV-ICP-MS	isotope dilution	11
natural gas condensates	0.5	GC-ICP-MS	introduction of sample in organic solvents	12
petroleum	0.78	ET-AAS	pre-concentration in graphite tube	13
gasoline	0.14	CV-AAS	microemulsion media	15
ethanol fuel	0.05	photo-CV-AAS	direct determination	16
gasoline	0.14	CV-GF-AAS	pre-concentration in gold column	36
ethanol fuel	0.05	CV-AAS	direct determination	this study

<sup>a</sup>GF-AAS, graphite furnace atomic absorption spectrometry; CV-ICP-MS, cold vapor inductively coupled plasma mass spectrometry; GC-ICP-MS, gas chromatography with inductively coupled plasma mass spectrometry; ET-AAS, electrothermal atomic absorption spectrometry; and AFS, fluorescence atomic spectroscopy.

The method precision in terms of repeatability was evaluated by analyzing three samples with different concentrations of Hg<sup>II</sup> (3, 13, and 23  $\mu\text{g L}^{-1}$ ). The relative standard deviation (RSD;  $n = 10$ ) for the recovery data for each level was calculated and found to be less than 3.5%, indicating that this method offers good precision.

Analyte recovery experiments were performed to evaluate the possibility for trace analyte determinations in four ethanol fuel samples acquired from different local vendors. Because of the lack of this type of reference material, analyte-enriched ethanol samples prepared in the laboratory were used. For all samples, the concentrations of the analytes of interest were below the LOQ of the method. Thus, the four samples were spiked with 3, 10, and 15  $\mu\text{g L}^{-1}$  Hg<sup>II</sup>, which resulted in a recovery range of 84–108% (Table 3), indicating a reasonable accuracy.

**Table 3. Relative Recovery for the Commercial Ethanol Fuel Samples to the Proposed Method<sup>a</sup>**

sample	Hg <sup>II</sup> added ( $\mu\text{g L}^{-1}$ )	Hg <sup>II</sup> found ( $\mu\text{g L}^{-1}$ )	recovery (%)
1	≤LOD		
	3	3.2 ± 0.06	106 ± 2.2
	10	10.4 ± 0.20	104 ± 1.9
	15	15.5 ± 0.12	103 ± 0.8
2	≤LOD		
	3	2.5 ± 0.01	84 ± 0.7
	10	9.3 ± 0.10	93 ± 1.1
	15	15.5 ± 0.35	103 ± 2.4
3	≤LOD		
	3	2.8 ± 0.13	92 ± 2.2
	10	10.2 ± 0.39	102 ± 1.8
	15	15.2 ± 0.32	101 ± 0.9
4	≤LOD		
	3	3.0 ± 0.08	101 ± 1.5
	10	10.8 ± 0.1	108 ± 0.8
	15	15.2 ± 0.5	101 ± 1.1

<sup>a</sup>LOD = 0.05  $\mu\text{g L}^{-1}$ . Replicates:  $n = 3$ .

## 4. CONCLUSION

The results presented in this paper clearly demonstrate that the CV-AAS method can be employed for the direct determination of Hg<sup>II</sup> in ethanol fuel samples. The carrier solution was HCl (5 mol L<sup>-1</sup>), and NaBH<sub>4</sub> (0.4%, w/v) was used as reducing agent. Ethanol fuel samples were prepared simply by forming a 2-fold diluted solution in water. This method is simple and fast (45 samples per hour) and does not require the sample to undergo harsh or time-consuming pretreatment. The method showed good precision (<3.5%), and a low LOD was obtained (0.05  $\mu\text{g L}^{-1}$ ). Recovery tests on analyte-spiked commercial ethanol fuel samples provided satisfactory results. The observed interference effect of some ions decreased with an increase of the HCl concentration. Considering all of these advantages, this method represents an attractive technique for the determination of Hg<sup>II</sup> in fuel samples.

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### Notes

The authors declare no competing financial interest.

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