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SAND99-0925

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Printed April 1999

Sampling and Sensing Systems for High Priority Analytes

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Sampling and Sensing Systems for High Priority Analytes

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Abstract

This reports summarizes the results from a Laboratory Directed Research and Development effort to develop selective coatings for detecting high priority analytes (HPAs), such as chemical warfare (CW) agents and their precursors, in the presence of common interferents. Accomplishments during this project included synthesis and testing of new derivatized sol-gel coatings for surface acoustic wave sensors (SAWs). Surfactant modified and fluoroalcohol derivatized sol-gel oxides were coated onto SAW devices and tested with volatile organic compounds (VOCs). These modified sol-gel coatings improved SAW sensitivity to DMMP by over three orders of magnitude when compared to standard polymeric coatings such as polyisobutylene and by over two orders of magnitude compared with polymers tailor made for enhanced sensitivity to phosphonates. SAW sensors coated with these materials exhibit highly sensitive reversible behavior at elevated temperatures ($>90^{\circ}\text{C}$), possibly leading to low detection levels for semivolatile analytes while remaining insensitive to volatile organic interferants. Additionally, we have investigated the use of reactive polymers for detection of volatile and reactive CW agent precursors (Chemical Weapons Convention Schedule 3 Agents) such as phosphorous oxychloride (POCl_3). The results obtained in this study find that sensitive and selective responses can be obtained for Schedule 3 agents using commercially available polymers and chemical guidelines from solution phase chemistry.

Keywords

Chemical sensor; chemical warfare agent; CW agent; sol-gel chemistry; polymer film; surface acoustic wave; SAW.

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Background

There are a wide variety of applications that require sensitive (sub-ppb) detection of particular compounds in real-world environments containing potentially-interfering compounds at significantly higher concentrations. For example, detection of CW agents or explosives can be critical during military operations or counter-terrorism activities. For many of these applications, small, portable systems are needed, which favors the use of low-power microfabricated chemical sensors and sensor arrays. In our work on environmental monitoring systems, we demonstrated high degrees of chemical discrimination using arrays of polymer-coated surface acoustic wave (SAW) sensors. We have also explored the use of novel microporous hydrophobic oxides as chemically-selective coating materials and have demonstrated trace (< 100 ppb) detection levels. In addition, we have shown that sampling systems, placed upstream from the sensor array, can dramatically enhance the performance of the sensors, both in terms of lower detection levels and improved chemical discrimination. Thus, sub-ppb detection levels of volatile organics now appear possible with this technology. Since the target HPAs are typically less volatile, they are detectable at even lower levels than the volatile organics studied previously.

Previous sampling systems consisted of a pump to capture a vapor sample and an adsorbent preconcentrator to collect the analyte of interest and then release it into a concentrated pulse upon heating. By proper selection of the adsorbent material, the analyte of interest is concentrated while other species are not collected or are trapped irreversibly, simplifying the chemical matrix sent to the sensor array. Using the porous polymer Tenax, for example, toluene is effectively concentrated while more volatile solvents like hexane are not collected. In addition, we demonstrated that during a controlled heat cycle, different species are released at different times (temperatures), enhancing the chemical discriminating power of the sensor array. Another advantage of this sampling system is that concentrated analyte pulses are presented to the array so that the response peaks can be quantified in the presence of sensor drift. This inherent drift compensation coupled with the preconcentration factors achievable have yielded detection levels more than 1000 fold lower than those obtained with standalone sensors.

Although the HPAs to be investigated have some unique chemical properties (reflected in their biological activity or explosive potential) that can be used to advantage in their selective detection, many would be irreversibly retained on sampling system hardware and on the adsorbents used for VOCs due to their low volatility. Thus, this project focused on redesigning and optimizing our sensor system components for the rapid, sensitive and selective detection of several HPAs.

A key component of the sensing system is the set of SAW sensor coatings used in the array. The performance of the SAW sensor is dictated by the partitioning of the vapor analyte into the sensor coating material, which can be quantified in terms of the partition coefficient K -- the ratio of the concentration in the coating to the gas phase concentration. A high K value indicates sensitive detection. Two factors affect the magnitude of the K value for an analyte - its volatility and its physicochemical interaction with the sensor coatings. Since partitioning is greater for less volatile vapors, K values tend to increase with decreasing volatility. Thus, very sensitive detection of the HPAs is expected due to their low volatility. Partitioning is also influenced by the specific chemical interactions between the analyte molecule and the coating material. Thus, selective detection can be achieved by using coating materials that have chemical groups that will interact with particular groups on the analyte. For example, explosives such as trinitrotoluene (TNT), which contain nitro groups substituted on an aromatic ring, will be preferentially attracted to sensor coatings containing tertiary amines and/or aromatic substituents. Finally, the physical structure of the sensor coating material can also affect K values. We have demonstrated that microporous oxide coatings prepared by a sol-gel process can provide K values that are 100 times larger than more conventional polymeric coatings for a given set of vapors by virtue of their pore structure and high surface area.

Introduction

The focus of this project was to redesign current array-based sensing systems by synthesizing sensitive and selective coatings for detecting high priority analytes (HPAs), such as CW agents, CW precursors, and explosives, in the presence of common

interferants. Since the target HPAs generally have low volatility or have high volatility combined with chemical reactivity, their analysis requires modifications in adsorbent materials used for sample preconcentration stages as well as in SAW sensor-array coatings. This materials optimization is facilitating the development of low-power, microanalytical systems (chemistry laboratory on a chip or μ ChemLabTM) that can provide rapid, sensitive, and selective detection of these HPAs in truly miniaturized field-deployable units. Specifically, adsorbent preconcentrator and SAW array detection coatings will be discussed. Spin-off applications in environmental monitoring and industrial process control are likely for other classes of semi-volatile chemicals (e.g., pesticides, sludges) that are notoriously difficult to monitor.

Surfactant Templated Sol-Gel Coatings

Coating Preparation: Using sol-gel chemistry [1], we have been successful in the synthesis of high surface area silica thin films ($>1000 \text{ m}^2/\text{g}$) with controlled pore size ($\sim 2\text{-}3 \text{ nm}$) and site specificity for the adsorption and desorption of dimethyl methyl phosphonate, DMMP, a nerve agent simulant that has a phosphonate functionality and a vapor pressure similar to soman. The thin film surface area and pore size were derived from the evaporation-induced co-assembly of silica and a surfactant (hexadecyl trimethyl ammonium bromide) followed by pyrolysis [2]. An example of this unique film microporosity is shown in Figure 1. Hydrophobic surfaces are prepared using sol-gel silica monomers of 90-95 mole percent tetraethyl ortho silicate and 5-10 mole percent of an octyl or octadecyl substituted silane. These are then annealed at 400°C in nitrogen. Hydrophilic surfaces are prepared by annealing at 400°C in air. DMMP site specificity results from subsequent silica surface modification of a hydrophilic film with a hexafluoroalcohol (HFA) containing sol-gel monomer. In-house synthesis of this HFA monomer was a significant accomplishment for this project. As shown in Figure 2, the hexafluoroalcohol moiety is thought to serve two important purposes: (1) the hydroxyl group, having two adjacent trifluoromethyl groups, inductively promotes enhanced hydrogen bonding to $\text{P}=\text{O}$ groups, i.e., DMMP and, (2) the hydrophobic fluoro groups significantly minimize the coating's sensitivity to water vapor as an interferant.

Figure 1. Transmission electron micrograph of uniform micropores in surfactant templated sol-gel thin film oxide.

Figure 2 - Silica surface modification with hexafluoroalcohol moieties for the adsorption and desorption of organophosphonate compounds.

Film Evaluation Using SAW Devices - Selectivity and sensitivity of coatings for the adsorption of chemical agents can be effectively tested using a surface acoustic wave (SAW) sensor as a mass detector. SAW devices were prepared by dip coating or spray casting quartz SAW devices designed to oscillate nominally at 100 MHz. SAW devices consist of a piezoelectric substrate, typically quartz, and two interdigitated transducers formed by photolithographic patterning of a thin metal layer. Application of an alternating voltage to the input transducer generates an alternating strain field that launches a surface acoustic wave that travels along the substrate surface before being converted back into an electrical signal by the output transducer. The velocity and attenuation of the propagating wave are very sensitive to properties, such as mass and viscoelasticity, of thin films formed on the device surface. For example, increases in surface mass loading cause decreases in wave velocity that can be used to detect picogram mass changes [3].

Sol-gel coated SAW devices were tested under two different protocols. Selectivity tests were performed using a pair of volatile organic compounds (VOCs) that exhibited differences in sorption characteristics based upon hydrogen-bond acidity and basicity. These selectivity tests are summarized below in Table 1. A second set of experiments was designed to test for the adsorption efficiency for DMMP. This second set of results is shown in a series of graphs under the DMMP discussion.

VOC Testing- Organophosphonate nerve agents are relatively polar molecules.

Specifically, these agents are known to have significant hydrogen-bond basicity that results in strong interactions with hydrogen-bond acidic materials. Two VOCs were chosen to study the sorption selectivity of the sol-gel coatings since these chemicals provide rapid and reversible responses on these coatings. Tetrachloroethylene (PCE), a relatively non-polar analyte with no hydrogen bonding potential, was tested in comparison with acetone, a polar molecule exhibiting a large hydrogen-bond basicity. Tests were performed by exposing the SAW device to a stream of gas and measuring the frequency shift of the attendant acoustic wave. Results in Table 1 show the selectivity gains noted for sol-gel coated SAW devices. Results from a previously synthesized

hydrophobic microporous oxide coating (a phenyl modified two step acid catalyzed coating with an approximate pore size of 0.8nm) are shown for comparison purposes. This microporous coating had an acetone response that was 20% of the PCE response. This result is consistent with the fact that the microporous coating is relatively hydrophobic and shows little preference for the polar acetone. The larger response to PCE was primarily due to it's lower vapor pressure allowing the equilibrium sorption to be higher on the surface of the SAW. Surfactant templated (ST) sol-gel coatings with larger pores (2-3nm) exhibited slightly increased selectivity for acetone while the greatest gains in selectivity were for the fluoroalcohol modified sol-gel coatings. The strong hydrogen-bond interactions with the fluoroalcohol-modified oxide-coated SAW device is seen in a 200-fold improvement in the acetone:PCE selectivity over the phenyl modified microporous coating.

Table 1. Selectivity of Coatings to Acetone and PCE (100MHz SAW Devices)

Sol-gel Coating	PCE Response Frequency Shift (Hz)	Acetone Response Frequency Shift (Hz)	Selectivity Acetone:PCE
55% Phenyl (A2)	-24600	-6080	0.2
Hydrophobic (ST)	-2500	-6820	2.7
Hydrophilic (ST)	-1450	-5750	4.0
Hexafluoroalcohol (swelled) (ST)	220	-1840	8.3
Hexafluoroalcohol (ST)	62	-2540	41.0

DMMP Testing – Although results from the VOC testing indicated significant improvements in selectivity for volatile polar molecules, realistic tests with the films would necessarily answer the question of nerve agent sorption and selectivity. For this reason, we designed and built a vapor test system that allows us to generate ppb levels of organophosphonate compounds such as DMMP. Using this system, the oxide-coated

devices were exposed to differing concentrations of DMMP. As part of our baseline testing for this class of compounds we used a specially developed hydrogen bond acid polymer coating (provided by Jay Grate from Pacific Northwest National Laboratory) that was highly selective and sensitive to phosphonate esters such as DMMP. Figure 3 shows the results of the polymer coating to various concentrations of DMMP. The hydrogen bond acid polymer coating gives approximately 1 Hz/ppb of DMMP at 50°C (this compares with 1 Hz/ppm of DMMP using a hydrocarbon polymer such as polyisobutylene (PIB)). Tests of the ST coated sol-gel coating showed that this film was 30 times more sensitive to DMMP than the hydrogen-bond acid polymer at 50°C (see Figure 4.) Note also that the ST sol-gel reacted rather irreversibly to the DMMP at 50°C. Although the film exhibits a degree of irreversibility at 50°C, the ST sol-gel shows excellent reversibility at 90°C (see Figure 5). It was found that the sol-gel coatings would need to be operated at elevated temperatures to exhibit reversible behavior. This irreversibility is, of course, a highly desirable quality of an adsorptive preconcentrator using selective films for sorption of high priority analytes such as nerve agents. The agents can be sorbed during sampling and then thermally desorbed onto other components of an analytical device for detection. Thus, the films can be adapted and operated for use on preconcentrator and detection hardware.

Figure 6 shows the results of a of DMMP adsorption onto a hexafluoroalcohol modified ST film at 100°C. These results indicate that the sensitivity to DMMP is slightly enhanced with this treatment. Table 2 gives a summary of the DMMP sorption amount (as measured by frequency shift) for various films at different conditions.

Figure 3. DMMP response for hydrogen bond acid polymer coated SAW device at 50°C.

Figure 4. DMMP response for surfactant templated (ST) sol-gel coated SAW device at 50°C.

Figure 5. Reversible response to DMMP for surfactant templated sol-gel coated SAW device at elevated temperature (90°C).

Figure 6. DMMP response for SAW device coated with ST sol-gel modified with hexafluoroalcohol (100°C).

Table 2. Sensitivity to DMMP for Various Coatings (100 MHz SAW Devices)

Coating	DMMP Response Frequency Shift (Hz/ppb)
Hydrogen Bond Acid Polymer (25°C)	7
Hydrogen Bond Acid Polymer (50°C)	1
Surfactant Templated Sol-Gel (25°C)	100
Surfactant Templated Sol-Gel (50°C)	38
Surfactant Templated Sol-Gel (90°C)	4.2
HFA Modified ST Sol-Gel (100°C)	10

It is obvious from Table 2 that the surfactant templated sol-gels are highly sensitive to DMMP adsorption. This effect is relatively irreversible at room temperature as shown in Figure 7, but demonstrates the utility of these films as preconcentrating membranes. A serendipitous aspect of this phenomenon is that many interferants, being compounds with higher vapor pressure, should have reduced affinity for the coating at elevated temperatures while excellent sensitivity to DMMP sorption is maintained.

Figure 7. Room temperature adsorption of DMMP using surfactant templated sol-gel coating and varying flows of a 220 ppb concentration.

Thus, these films appear to have the potential to provide 10-100 fold greater sensitivities as compared with the best polymeric materials as well as providing unique chemical selectivity based on both the surface chemistry and the size and shape of the porosity. Still further sensitivity gains are shown for the surfactant templated ST sol-gel that has been modified with HFA. The results of DMMP testing with a SAW device coated with the HFA modified sol-gel show a marked increase in sensitivity (even though the test temperature was 10°C higher) and are consistent with the selectivity data shown in Table 1.

Conclusions and Future Recommendations:

Surfactant Templated Sol-Gel Coatings

In conclusion, much progress has been made both in selectivity and sensitivity for modified sol-gel coatings for CW agent detection. **Selectivity was improved by over 2 orders of magnitude while sensitivity gains were estimated to be greater than 1000 times a non-selective yet standard polymeric coating such as polyisobutylene (PIB).**

Due to the random distribution of hexafluoroalcohol (HFA) sites on the silica surface, the current affinity of HFA thin films towards organophosphonates (DMMP) relies primarily on hydrogen bonding interactions (Figure 2). Further discrimination of the target molecule from a plethora of non-target interferents may be enhanced by designing molecular recognition sites on the silica surface via a template imprinting approach. For example, recognition sites could be generated by allowing the HFA and DMMP (template) to self-assemble in the sol and film formation process creating a thermodynamically favored orientation of the HFA sites around the template. Subsequent template removal results in a cavity with specific dimensions and stereochemistry for the target molecule.

Additional chemical modification of the oxide surface may lead to materials with high selectivity towards high volatility, high reactivity analytes such as mustard gas and chlorinating agents. For example, transition metals (Ni, Cu, Pd, Rh and Fe) have high

affinity towards sulfide and amine compounds (common functional groups in mustard gas) and may be incorporated into the silica matrix in their reduced form. We hope to be able to sense irreversible adsorption of sulfides and amines (as occurs in catalyst poisoning) as a characteristic SAW response using this type of material.

Reactive SAW Sensor Coatings for Schedule 3 Agents

A second series of coatings were prepared and tested with compounds known as Schedule 3 agents. These films were primarily experimental polymeric films. Chemicals included in the Schedule 3 list of the Chemical Weapons Convention are dual-use and produced in high volume. Many of the chemicals are used as chlorinating and dehydrating reagents in syntheses of commercial products (e.g., drugs, plastics, etc.). Compounds such as phosphorus oxychloride (POCl_3), phosphorus trichloride (PCl_3), phosphorus pentachloride (PCl_5), and thionyl chloride (SOCl_2) are efficient at forming alkyl halides, acid chlorides, cyano groups, phosphates, aryl halides, aryl aldehydes, heterocycles, as well as performing other important reactions [4]. The majority of these reactions are conducted in solution at or near room temperature.

The high reactivity and specificity of reaction of these chemical agents to certain functional groups was considered in developing new SAW sensor materials for Schedule 3 agents. Thin polymer films containing alcohols, phenols, carboxylic acids, pyridines, and amides are good candidates for the selective reaction with the above mentioned agents. Subsequent reaction should generate significant changes in the polymer film's weight and, more significantly, the film's viscoelasticity due to the changes in intra- and inter-molecular hydrogen bonding, and changes of polarity at the functional sites. Such changes on the sensor film coating will be readily detected by the SAW device. However, the basis of the reactivity of the chemical agents is derived from what is understood from solution phase chemistry leaving many unknowns in the gas phase.

We have prepared a set of polymer thin films with various functional groups to test material response to gas phase Schedule 3 agents. The polymer pendant groups were chosen based on the reactivity of the agents to specific functional groups. Figure 8 lists

functional group transformations that are specific to the agents PCl_5 , POCl_3 , PCl_3 , and SOCl_2 . The transformations (1), (2), and (4) change strong hydrogen bond donors to hydrogen bond acceptors. Transformation (3) alters hydrogen bond donor as well as acceptor sites, but more significantly alters the polarity of the functional site. Salt formation of pyridine from reaction (5) introduces ionic charge to the polymer. The specificity of the agents to each of the listed reactions is tabulated in Table 3.

Figure 8. Functional group conversions using chemical agents listed in Table 3.

Table 3. Reactivity of Schedule 3 agents to specific functional groups

Reaction	PCl_5	POCl_3	PCl_3	SOCl_2
1	●	●	●	●
2	●		●	●
3	●	●		●
4		●		
5		●		

The functionalized polymers listed in Table 4 were spin cast onto SAW devices forming sub-micron thin films. Dry polymers were dissolved in suitable good solvents to the concentrations indicated in the table. Polymers obtained as solutions were diluted to desired concentrations. A small volume (100 – 200 μL) of the homogeneous polymer solution was spin cast at 3000 rpm for 20 seconds on the SAW device to yield an optically smooth coating. After curing overnight at reduced pressure (20 inches of Hg) and 60°C, the thickness of selected polymer films were determined using a Dectac profilometer and the results are reported in Table 4.

Table 4. Spin cast conditions and characterization of polymer films on SAW device

Polymers	Solvent	Solution conc. for spin cast	Film thickness	Response to POCl_3
Polystyrene	THF	200 mg/10 mL	160 nm	no
Polymethyl methacrylate	THF	200 mg/10 mL	120 nm	no
Polyvinylalcohol	50% MeOH/ H_2O	200 mg/10 mL	70 nm	no
Polyacrylic acid/ polyacrylamide	50% MeOH/ H_2O	200 mg/10 mL	170 nm	yes
Poly(4-vinylpyridine)	MeOH	200 mg/10 mL	---	yes
Poly(4-vinylphenol)	MeOH	200 mg/10 mL	---	no
Polyhydroxyethyl methacrylate	EtOH	2% v/v	---	no
Polyacrylic acid 90K	H_2O	2% v/v	---	no
Polyacrylic acid 50K	H_2O	2% v/v	---	no
Polyvinylphosphonic acid	H_2O	200 mg/10 mL	---	no

The coated SAW devices were tested against various interferants and the target agent POCl_3 . Polystyrene and polymethylmethacrylate, having no reactive groups, were prepared as control sensor materials. Alcohol containing polymers, polyvinyl alcohol

and polyhydroxyethyl methacrylate, should follow reaction 1 producing alkyl chlorides or reaction 4 yielding phosphate esters. The amide containing polymer, polyacrylic acid/polyacrylamide, may produce nitriles following reaction 3 while the phenol containing poly(4-vinylphenol) could yield phosphate esters as in reaction 4 and the poly(4-vinylpyridine) should follow reaction 5. The carboxylic acid moieties of polyacrylic acid should be unreactive to POCl_3 producing no response for the thin film.

Only two of the polymer films gave strong and selective responses to ppbv levels of POCl_3 : the polyacrylic acid/polyacrylamide copolymer (see Figure 9) and poly(4-vinylpyridine). No response was observed from the control films nor for the rest of the functionalized polymers to POCl_3 . Of the functionalized polymers expected to respond to the agent, the hydroxy containing polymers (phenols and alcohols) were surprisingly non responsive. Based on solution phase studies [5] of alcohols reacting with POCl_3 , the polymers were expected to react efficiently at room temperature to give phosphates as in reaction 4 [5]. Alkyl halide formation (reaction 1) is also possible with the alcohols, although elevated temperatures are typically required [6]. Lack of response from the carboxylic acid polymers to POCl_3 was anticipated from their lack of reactivity in solution phase. The response thus observed from the polyacrylic acid/polyacrylamide copolymer film suggests that POCl_3 reacts with the amide groups producing nitriles as in reaction 3 [7]. The response was irreversible indicating that a strong interaction or a functional group transformation, such as nitrile formation, had occurred in the film. An observed response from the poly(4-vinylpyridine) film to POCl_3 suggests the formation of the pyridinium salt of reaction 5 [8]. Another possible route for the observed SAW response would be the capture of the agent by the strong Lewis base pyridine to the strong Lewis acid POCl_3 . A reversible response found with this film suggests reversible host-guest interactions are involved, such as an acid-base interaction, rather than covalent bond formation as in reaction 5. Further characterization of the responding films to POCl_3 exposure will be conducted to identify and characterize the sites of reactions or interactions.

The sensors were also tested against several interferants to gauge the selectivity of the sensor material. Results of the tests are shown in Table 5. The materials were exposed to 100 ppmv of xylene, octane, tetrachloroethene (PCE), isopropanol (IPA), and methylethylketone (MEK). For the highly polar acid and alcohol containing films, the lack of interaction with the non-polar hydrocarbons is reasonable. Three of the four interferants showed responses to the polyacrylic acid/polyacrylamide copolymer, but unlike phosphorus oxychloride, these responses were reversible.

Table 5. SAW sensor response to interferants and POCl₃

Polymers	POCl ₃	Xylene	PCE	Octane	IPA	MEK
Polystyrene	†					
Polymethyl methacrylate	†					
Polyvinylalcohol	†	†	†		†	†
Polyacrylic acid/polyacrylamide	●	●	†		●	●
Poly(4-vinylpyridine)	●	●	●	●		●
Poly(4-vinylphenol)	†	†	†	†		†
Polyhydroxyethyl methacrylate	†	●	●	●		●
Polyacrylic acid 90K	†	†	†	†		†
Polyacrylic acid 50K	†	†	†	†		†
Polyvinylphosphonic acid	†	†	†	†		†

● – response, † - no or little response, blank – no test performed.

Figure 9. Response to low-level challenge (100 ppbv) of POCl_3 for SAW devices coated with a polyacrylic acid/polyacrylamide copolymer and with polyvinyl alcohol.

Conclusions and Future Recommendations:

Reactive Coatings for Schedule 3 CW Agents

The results obtained in this study find that selective responses can be obtained for Schedule 3 CW agents using commercially available polymers and chemical guidelines from solution phase chemistry. Unexpected results and trends found within the results offer valuable clues into the important interactions involved with gas phase analytes. For example, the reversible response of poly(4-vinylpyridine) to POCl_3 suggests acid-base interactions between the host film and guest agents rather than chemical reaction. In addition, the lack of reactivity of the alcohols in the film to POCl_3 may be a result of inefficient presentation of the functionality to the analytes. Further characterizations of the reacted films are needed to fully define the site of agent binding. Tests will also be performed on the films for the other Schedule 3 agents to determine their effect on material functionality from the gas phase. In considering materials for future sensor development, emphasis will be placed on functional group *interactions* rather than *reactions* with the agents for reversible and tailored selectivity in response.

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