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Short communication

Investigation of the storage stability of selected volatile sulfur compounds in different sampling containers

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Abstract

The suitability of various sample containers (i.e. standard Tedlar sample bags, black/clear layered Tedlar sample bags and Silcosteel sample cylinders) was examined for a gaseous multicomponent standard containing methylmercaptan, ethylmercaptan, dimethyl sulfide, ethylmethyl sulfide, 2-propylmercaptan, 1-propylmercaptan, 2-butylmercaptan, diethyl sulfide and 1-butylmercaptan (1 mg/m^3 each in nitrogen). In the black/clear layered Tedlar sample bags, significant losses (up to 10% for methylmercaptan as the most critical component) were observed after 2 days, whereas in the standard Tedlar sample bags the recovery of methylmercaptan was approximately 90% even after 1 week. The Silcosteel sample cylinders were suitable for sampling of volatile sulfur compounds with respect to the stability of the analytes, but the recoveries exceeded 100% especially for the higher boiling compounds, which was attributed to enrichment effects on parts of the sampling system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Knowledge of the type and concentration of volatile sulfur compounds (VSCs) in natural gas is of great importance to the industry for several reasons. On the one hand, these compounds poison catalysts, cause corrosion and contribute to environmental pollution (formation of acidic rain), which makes the reduction of natural occurring VSC concentration mandatory. On the other hand, odorous sulfur compounds are added to the odorless natural gas as

warning agents for the consumer for safety purposes [1]. The odourisation process requires a fast and accurate analytical method for the control of the concentrations of the sulfur compounds in the raw gas and of the odour level in the odourized gas, since excessive concentrations of these compounds result in an elevated number of consumer complaints [2].

The analysis of VSCs is particularly difficult, since they tend to adsorb onto surfaces and, in the case of mercaptans, may undergo partial oxidation [3,4]. Therefore, all the materials which the VSCs come into contact with during sampling and analysis should be as inert as possible. In contrast to air samples, where the concentrations of the VSCs are in the lower $\mu\text{g/m}^3$ – or even in the ng/m^3 – range

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and therefore the analytes have to be preconcentrated prior to analysis [3], VSCs are present in natural gas samples in the mg/m^3 range and therefore are usually analyzed directly after collection in suitable containers. To maintain sample integrity, analyte losses due to adsorption, oxidation or diffusion through the walls of the containers must be prevented.

Sample bags made of Tedlar film, which is a polyvinylfluoride material, are usually chosen in industrial routine analysis because of their ease of handling, inertness and comparatively low price. Lau examined the stability of a gas mixture of six sulfur compounds at the ppb (v/v) (ppbv) concentration level in a 5-l Tedlar air sampling bag over a period of 21 days [5]. Half-lives of the six sulfur gases were as follows: SO_2 (0.02 day), H_2S (10 days), ethylmercaptan (EtSH; 25 days), methylmercaptan (MeSH; 29 days), CS_2 (58 days) and COS (100 days). The author concluded that although Tedlar bags are not suitable for SO_2 and H_2S , the stability of the other compounds is good enough to collect ambient air samples in Tedlar bags and send them to laboratory for analysis. Stein and Narang examined the stability of a mg/m^3 mixture of EtSH, propylmercaptan (PrSH; the isomer was not stated), *tert.*-butylmercaptan (t-BuSH), 2-BuSH and 1-BuSH, which was prepared by injecting a gaseous mercaptan mixture into a 10-l Tedlar bag, that had been filled with nitrogen [6]. The concentrations of the gas mixture were stable for 10 days but were also found to be significantly lower than the value expected from the direct analysis of an equal amount of methanolic standard of the VSCs. The authors explained this undervaluation by possible deficiencies of the procedure used for the preparation of the gaseous standards (adsorption or volatilization losses). Despite these losses, linearity was obtained from various concentrations of bag standards. Therefore, the authors concluded that reliable quantitation can still be obtained by using this method by applying a correction factor to the bag standards.

Glass or metal sampling bulbs are generally not accepted, since the stability of VSCs was found to depend on the oxygen and water content of the sample [7]: Devai and DeLaune determined the influence of the balance gas matrix and humidity (dry nitrogen, dry air and humid air) on the recovery

of a ppm (v/v) mixture of five VSCs (H_2S , COS, SO_2 , CS_2 and MeSH) collected in glass sampling bulbs. In dry nitrogen, analyte losses were less than 5% after 24 h, after 48 h significant losses of 10–35% were observed for CS_2 , MeSH and DMS. In dry air, the mixture remained stable for 3 h, after 24 h losses of 10–20% occurred for all components except H_2S , which remained stable during that period. In humid air, the changes in concentration were considerable even after 1 h: the losses ranged from 5% for COS, CS_2 and DMS to 35% for MeSH and 55% for H_2S . Since the oxygen and water content of natural gas is usually in the ppm range, glass sampling bulbs may still be an acceptable choice in routine analysis.

A revolutionary development in passivation technology was achieved by the Silcosteel treatment, which was commercially introduced in 1987. It bonds a layer of silica onto the inner surface of stainless steel parts to make them unreactive to sulfur compounds. Stidsen et al. examined the stability of H_2S , COS, MeSH, EtSH, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS; 60 ppbv each in Nitrogen) in Silcosteel treated sample cylinders [8]. The recoveries exceeded 80% for all compounds after 24 h, after 70 h they exceeded 75% for all compounds except H_2S . These results demonstrated the superior performance of Silcosteel sample cylinders in comparison to untreated stainless steel cylinders.

An even more recent technology of passivation is the Sulfinert treatment, which allows sample storage of sulfur gases at the low ppbv level, which is not possible even on inert fused-silica based coatings [9]: Barone et al. showed that in Sulfinert treated cylinders an 11 ppbv mixture of H_2S and MeSH is stable for 14 days and a 1.5 ppbv mixture of these compounds is stable for 6 days.

In this paper, the stability of a gaseous multi-component standard is examined in three different types of vessels: Silcosteel sample cylinders, standard Tedlar sample bags and black/clear layered Tedlar bags (which combine a clear Tedlar film inside a layer of black Tedlar for light protection of light-sensitive compounds). Besides MeSH, EtSH and DMS, the list of investigated compounds also includes propyl- and butylmercaptans, ethylmethyl sulfide (EMS) and diethyl sulfide (DES). Although

some of these compounds are relevant due to their use in odorant mixtures, to our knowledge there has only one article been published so far [6] on their behavior in sample containers.

2. Experimental

2.1. Materials

The gaseous multicomponent standard used in this work was purchased from Sapiro (Monza, Italy). The components and their concentrations are given in Table 1.

The 12-l standard Tedlar sample bags and the 10-l black/clear layered Tedlar bags were obtained from SKC (Eighty Four, PA, USA), the 1-l Silcosteel sample cylinders were purchased from Restek (Bellefonte, PA, USA). For the stability study, two sampling containers of each type were used. For calibration, a 2-l standard Tedlar sample bag from Supelco (Bellefonte, PA, USA) was used.

2.2. Sampling

All three types of vessels were purged three times with argon (>99.996%) and four times with the multicomponent standard prior to sampling. The final pressure in the sample cylinders was 57 p.s.i. (1 p.s.i.=6894.76 Pa). Samples were stored in an air-conditioned room at 21°C exposed to daylight to study the influence of this factor.

Samples of 2 ml were taken periodically using a 5-ml gas-tight syringe (Hamilton, Reno, NV, USA), starting the first measurement immediately after the

containers had been filled. When taking aliquots of the sample in the Tedlar bag it was avoided to pierce the septum of the sampling port of the Tedlar bag in order to avoid the risk of leakage during storage. Instead, a silicon tube (3 mm I.D.) was connected to the fitting of the bag, the valve of the fitting was opened and the tubing was purged with the sample for approx. 1 min with a flow of at least 20 ml/min prior to sampling from this purged gas line. In contrast to this, the manifold used for the Silcosteel sample cylinders allows direct sampling, since a valve separates the sampling port, which is closed by a septum, from the sample cylinder.

2.3. Sample introduction, separation and detection

In order to have small peak widths and to avoid sample discrimination problems related to split injection, samples were injected into a laboratory-built thermodesorption/cryofocusing unit coupled directly to the analytical column. The thermodesorption/cryofocusing unit mainly consists of inert parts (made of Silcosteel and deactivated glass) to avoid analyte adsorption and artefact formation. Gas chromatography–atomic emission detection (GC–AED) analysis was carried out with a HP 5890 II gas chromatograph coupled to a HP 5921A atomic emission detector (Hewlett-Packard, Palo Alto, CA, USA). The parameters for sample introduction as well as the separation and detection parameters are given in Table 2.

2.4. Quantitation

Since the sensitivity of the analysis system increased slightly in the course of 1 day, it was calibrated two or three times per day. For calibration, a 2-l standard Tedlar sample bag was freshly filled with the gaseous standard prior to analysis.

The response of these measurements was taken as base for the calculation of the recoveries in the three different types of vessels. Every calibration and measurement of one data point was carried out threefold to obtain information on the repeatability of the method. The standard deviation of the recovery of one data point was calculated from the standard deviations of the peak areas of the calibration and of the data point itself by the law of error propagation.

Table 1
Composition of the gaseous multicomponent standard

Substance	ppm (v/v)	mg S/m ³	mg compound/m ³
MeSH	0.56	0.74	1.11
EtSH	0.42	0.56	1.08
DMS	0.42	0.56	1.08
2-PrSH	0.33	0.44	1.04
EtMeS	0.33	0.44	1.04
1-PrSH	0.33	0.44	1.04
2-BuSH	0.28	0.37	1.04
DES	0.29	0.39	1.10
1-BuSH	0.29	0.39	1.10

Table 2
Parameters of sample introduction, separation and detection

Cryofocusing time	20 min
Carrier gas flow through thermodesorption/cryofocusing unit	20 ml He/min
Cryofocusing temperature	−196°C
Desorption temperature	100°C
Coupling of thermodesorption unit	On column
Analytical column	GS-Q porous-layer open tubular (PLOT) (J&W Scientific, Folsom, CA, USA), 25 m×0.32 mm I.D.
Column flow	3 ml/min helium (>99.9996%)
Temperature program	60°C for 2 min, with 5°C/min to 130°C, with 30°C/min to 240°C, 2.5 min hold
AED total He flow	20 ml/min
AED reagent gases	2.1 bar O ₂ (>99.998%), 0.7 bar H ₂ (>99.999%)
Detection wavelengths	181 nm (sulfur), 193 nm (carbon)
Data acquisition rate	5 Hz
Transfer line temperature	290°C
Cavity temperature	300°C

Since it was not possible to separate 1-PrSH from EtMeS with the chosen chromatographic column (see Fig. 1), the sum of the peak areas of these two compounds was quantified.

3. Results and discussion

When the kinetics of adsorption or decomposition is followed, it is often useful to carry out regression analysis on the experimental data. In the case of the data presented in this study, however, the results of regression analysis were generally dissatisfying irrespective of the kinetic model that was assumed.

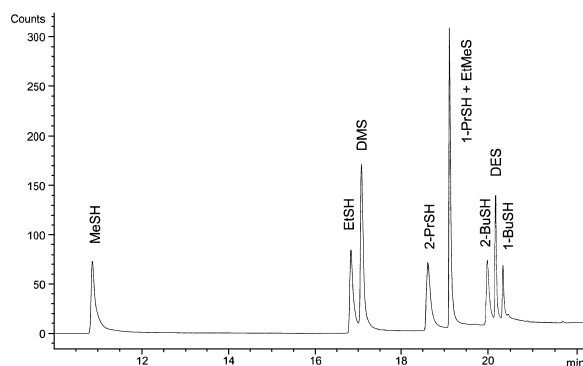


Fig. 1. Sulfur-selective chromatogram of the multicomponent standard (identification was carried out by injecting retention time standards).

Therefore, the trend test after Neumann was chosen as objective criterion to decide whether concentrations have decreased significantly in the course of the investigated period (see Table 3).

In the standard Tedlar sample bags, all components were recovered quantitatively after 1 h (Figs. 2–5, top). Neumann's test showed significant trends for MeSH in both bags and for DMS and DES in bag 1, the latter being caused by the high recovery after 1 h. At the end of the investigated period, losses of approx. 10% were also observed for EtSH in both bags and for DMS in bag 2 whereas the recovery of the other compounds was quantitative even after a storage period of 300 h. Light protection does not seem mandatory for the storage of VSCs.

In the black/clear layered Tedlar bags significant losses (up to 20–30% for the higher boiling C₃ and C₄ compounds) were observed already after 1 h (Figs. 2–5, middle). The concentrations, however, did not show a trend and remained practically constant over the remaining 14 days of storage. In contrast to this, initial sample losses of MeSH, EtSH and DMS did not exceed 10%, while the recoveries of these compounds continuously decreased over the storage period of 2 weeks to approx. 70%. The difference in the magnitude of sample loss (up to 20% for the higher boiling compounds) between the two individual bags is also quite remarkable, since similar effects were not observed in the standard Tedlar sample bags or in the Silcosteel sample

Table 3

Results of Neumann's trend test [a significant trend is observed at the 95% (99%) level when the value of the test variable is smaller than the 95% (99%) threshold value]

	Standard Tedlar sample bag		Black/clear layered Tedlar bag		Silcosteel cylinder	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
MeSH	<i>0.66</i>	<i>0.61</i>	<i>0.71</i>	0.92	2.19	0.60
EtSH	1.04	1.77	0.41	<i>0.65</i>	0.56	0.32
DMS	0.52	1.45	<i>0.90</i>	0.44	1.65	1.00
2-PrSH	0.97	1.92	2.40	1.07	<i>0.72</i>	0.46
1-PrSH+EMS	1.03	1.36	2.04	1.07	0.46	0.29
2-BuSH	1.19	1.09	1.05	1.31	0.44	0.26
DES	<i>0.74</i>	1.26	2.37	1.01	1.03	0.61
1-BuSH	1.39	2.03	1.36	1.49	0.33	0.22
Critical value ($P=0.99$)	0.5615	0.5615	0.614	0.5615	0.614	0.614
Critical value ($P=0.95$)	0.8902	0.8902	0.9359	0.8902	0.9359	0.9359

The significant values are printed in bold face ($P=99%$) or in italics ($P=95%$).

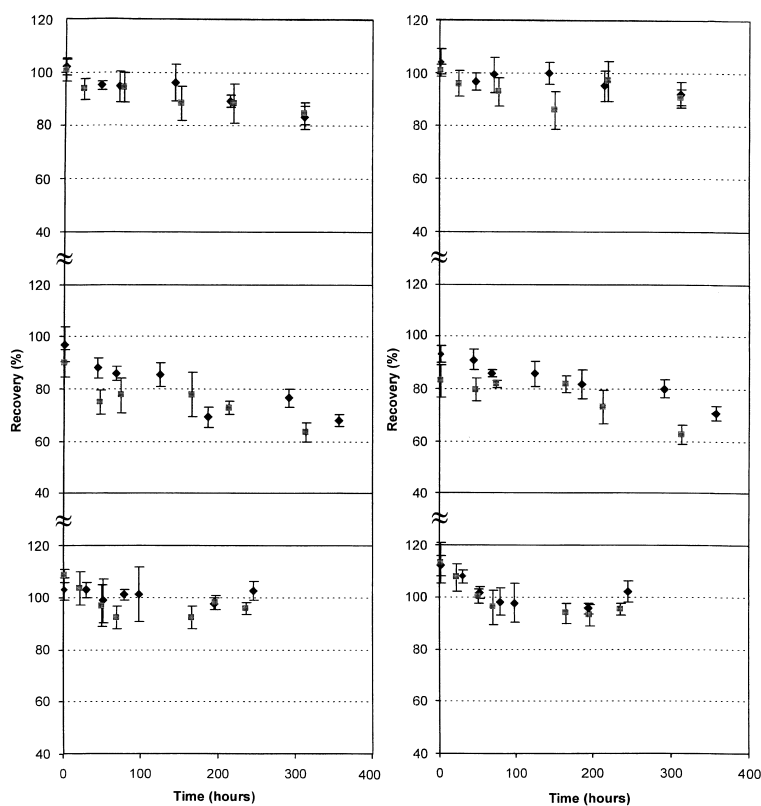


Fig. 2. Recoveries of MeSH (left) and EtSH (right) in standard Tedlar sample bags (top), black/clear layered tedlar bags (middle) and Silcosteel sample cylinders (bottom). Diamonds indicate container 1, squares indicate container 2.

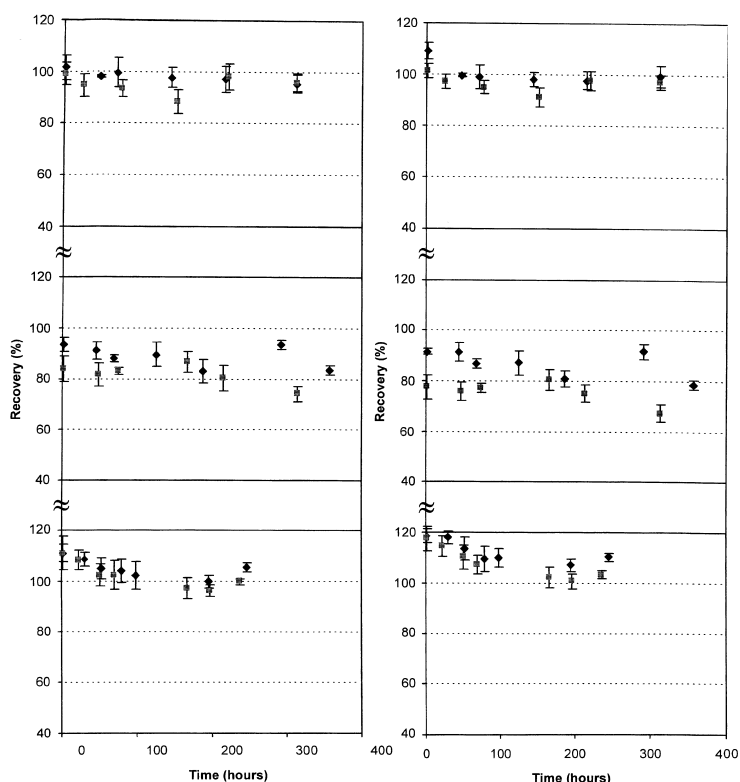


Fig. 3. Recoveries of 2-PrSH (left) and 1-PrSH+EMS (right) in standard Tedlar sample bags (top), black/clear layered tedlar bags (middle) and Silcosteel sample cylinders (bottom). Diamonds indicate container 1, squares indicate container 2.

cylinders. A possible explanation for these losses is the permeation of the analytes through the 50 μm thick inner layer of clear Tedlar into the black Tedlar, where they are adsorbed. The manufacturer of the bag states that the carbon black in the outer layer might adsorb some compounds as was observed with single layer black bags, but also claims that the inner layer of the bag should present an effective diffusion barrier and thus prevent adsorption losses [10].

In the Silcosteel sample cylinders the recoveries of all investigated compounds except MeSH in cylinder 1 were significantly higher than 100% for the first measurement (Figs. 2–5, bottom). During sample storage, however, the recoveries of the investigated VSCs decreased considerably with the exception of DMS and DES. In detail, this meant that the recoveries for MeSH (only in cylinder 2), EtSH, 2-PrSH and 1-PrSH+EMS compounds dropped by

approximately 10%, for 2-BuSH and DES by 20% and for 1-BuSH by 40%. Only the recovery of 1-BuSH in one of the two cylinders dropped below 95%. The reason for the initial over-estimation of the recoveries is not completely clear yet. As was discussed with the manufacturer of the cylinders, one possible assumption is that the inner surface had been primed during purging and later compounds were released from the primed surface due to the pressure drop in the sample cylinders [11]. To avoid this effect, a different sampling method was suggested that was already used by the supplier of the cylinders for performing the VSC stability tests reported above: the cylinders were evacuated, the standard was added and pressurized for dilution prior to analysis [11]. Other factors like enrichment effects in other parts of the analysis system, cannot be excluded. These effects form part of further work and will be presented elsewhere [12].

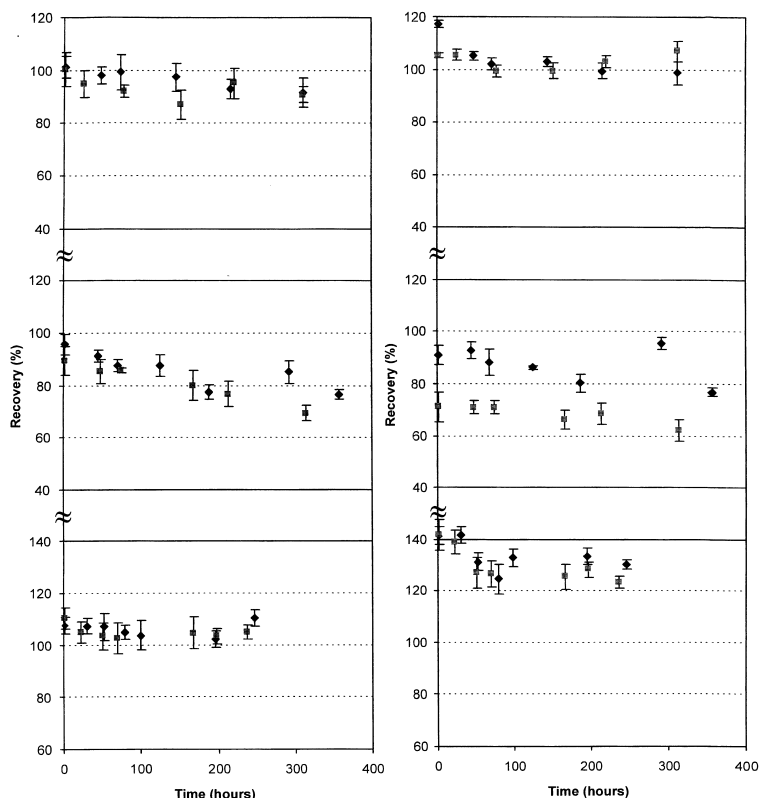


Fig. 4. Recoveries of DMS (left) and DES (right) in standard Tedlar sample bags (top), black/clear layered tedlar bags (middle) and Silcosteel sample cylinders (bottom). Diamonds indicate container 1, squares indicate container 2.

4. Conclusion

The stability of VSCs in the standard Tedlar sample bags is sufficient for routine analysis, because natural gas samples are usually measured within 24 to 48 h. Light protection is not necessary since the relevant VSCs are stable over this storage period. In contrast to this, the use of black/clear layered Tedlar bags results in significantly lower recoveries presumably due to uncontrolled adsorption of the VSCs to the black carbon filled Tedlar layer. The use of Silcosteel sample cylinders is also acceptable since they exhibit good performance as concerns the stability of MeSH, which is normally the most concentrated and at the same time the most reactive organic sulfur compound and thus most relevant for the further processing of natural gas. However, further investigations of the cause for the

initial overestimation of the VSC recoveries should be carried out before the cylinders are introduced to routine analysis.

Since the significant economic advantage of using standard Tedlar sample bags (they are about 40 times cheaper than a Silcosteel sample cylinder) is not offset by a compromised performance as concerns the stability of the VSCs, they seem to be the best choice for routine analysis.

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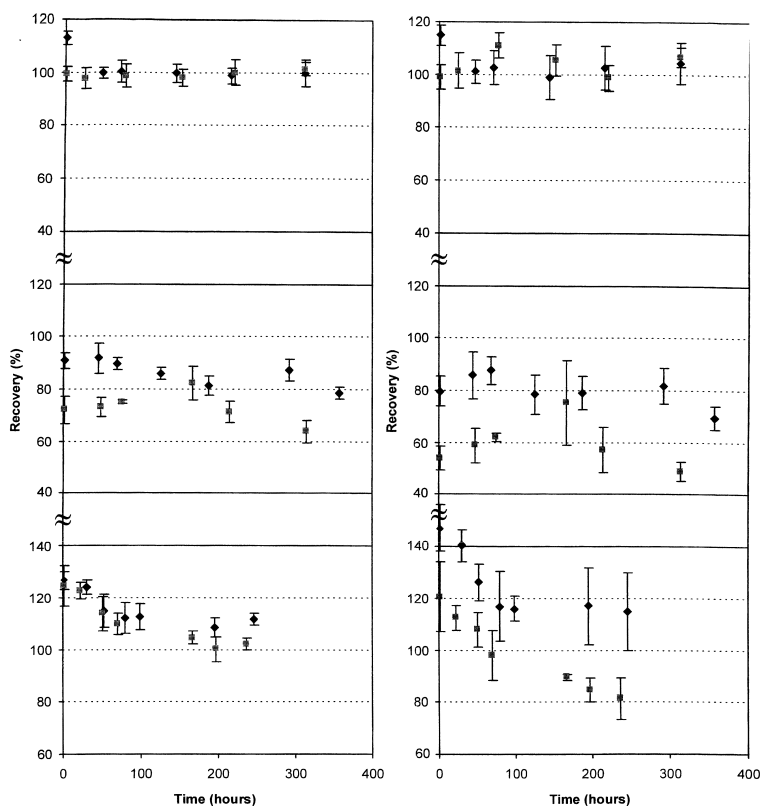


Fig. 5. Recoveries of 2-BuSH (left) and 1-BuSH (right) in standard Tedlar sample bags (top), black/clear layered tedlar bags (middle) and Silcosteel sample cylinders (bottom). Diamonds indicate container 1, squares indicate container 2.

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