

Making a case for regenerating gas chromatography liners in industrial wastewater screening

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INTRODUCTION

Anthropogenic activities, particularly of industrial nature, within the City of Los Angeles would contribute a significant amount of semi-volatile organic pollutants (SVOCs) into the city's coastal waters if left unchecked. In normal operations of the City, industrial wastewater discharges are guided into four wastewater treatment plants from where best management practices are combined with upstream pretreatment programs to remove as much SVOCs as possible before allowing the plants effluents into the sea.

Like other major coastal cities of the USA, the City of Los Angeles is required by the Clean Water Act to monitor the impact of this industrial wastewater discharges on the health of the sea, and to ensure that all discharges meet or exceed strict water quality standards.

To monitor the levels of SVOCs being discharged into the ocean, the City relies on the analytical strength of GC-MS systems. One component of a GC-MS which must be replaced frequently is the glass inlet liner found at the injection port of the GC. The unintended consequence of replacing many liners in the City's laboratories on a daily basis is accumulation of used liners.

OBJECTIVES

To address the laboratory accumulation of used gas chromatography liners in an environmentally friendly way and in a cost-effective manner: to accomplish this by searching for a robust regeneration protocol accomplishable by a simple series of off-the-shelf laboratory procedures without presenting undue burden to the City of Los Angeles.

MATERIALS & METHODS

Chemicals and materials – Pesticides-grade solvents (methanol, acetone, and dichloromethane) were purchased from Fisher Scientific; 5% DMDCS and GC-MS system suitability solution were obtained from Supelco Analytical. The system suitability solution was diluted to $50 \text{ ng } \mu\text{L}^{-1}$ before use. Liners (dual-taper direct-connect, 4 mm I.D.) purchased from Agilent.

Liner Regeneration – Two hundred and eighty-eight (288) used inlet liners were randomly selected and sonicated in methanol, acetone, and dichloromethane in that order for 30 min, baked at 500°C for 12 h, sonicated and deactivated in 5% DMDCS overnight at room temperature. This was followed by rinses (3×) with dichloromethane and drying at 100°C for 15 min before use. New liners were deactivated for 15 min in DMDCS followed by methanol, acetone, and dichloromethane rinses.

CCV sample mixture preparation – The recovery of the daily continuous calibration-verification standard mixture (CCV) solution, the midpoint of a 9-point concentration calibration curve, was used as the basis of testing the fidelity of liner regeneration. The solution was prepared daily by mixing 20 μL aliquot of each of the following stock solutions from Supelco Analytical and bringing the mixture up to 1 mL in dichloromethane: TCL Base-Neutrals,

SS TCL Benzidines Mix, SSTCL Phenols Mix, 8270 Surrogate Standard, TCL Hazardous Substances Mix, and SS TCL Polynuclear Aromatic Hydrocarbons Mix. The resulting mixture contained 61 organic compounds considered priority pollutants by US EPA. Thirteen of these were calibration check compounds, four were system performance check compounds, and six were surrogate compounds. For quantitation, six internal standards (1,4-dichlorobenzene, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, Supelco Semi-volatile Internal Standard Mix) were added to samples before GC-MS analyses.

GC-MS analyses – The CCV analyses (as part of sample batches) were performed according to US EPA Method 625. A batch of samples were analyzed in the following order: instrument blank, method blank, laboratory control (CCV), matrix spike, matrix spike duplicate, instrument blank, and IW samples. The CCV data were then extracted and used as the basis of this report. To minimize variation, a single GC-MS was used for all analyses employing regenerated liners.

Data validity and interpretation – Statistical validity of data analysis was assumed on the basis of the multiplier effect of measuring 61 unique compounds in 11 randomly selected regenerated liners (for a total of 1364 data points). Boxplots were used to gauge data distributions.

To determine the type of data structure or additional properties present, the 1364 data points were examined by scatter plot and by the Bland-Altman plot. PAST and Microsoft Excel 2010 software were used for statistical analyses.

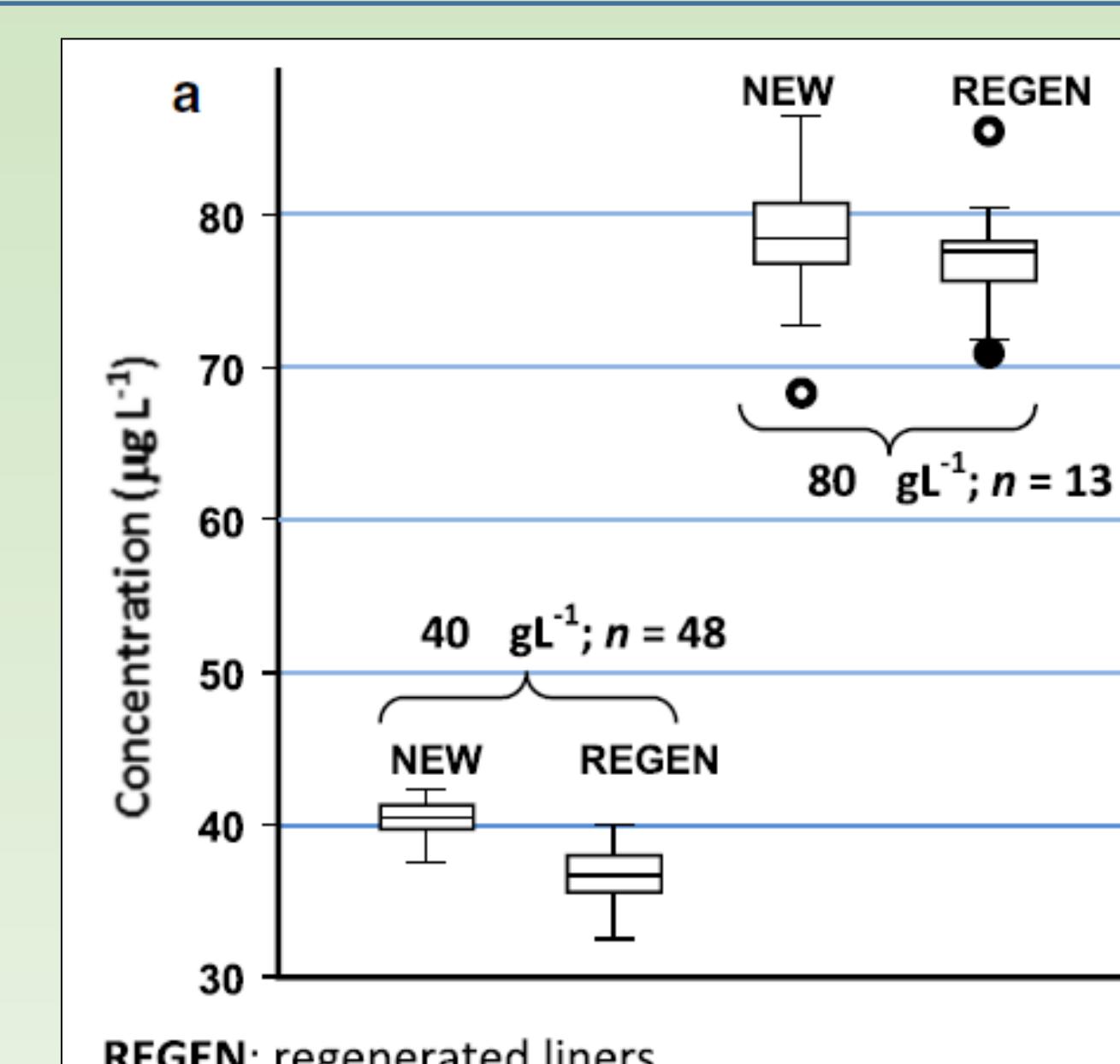
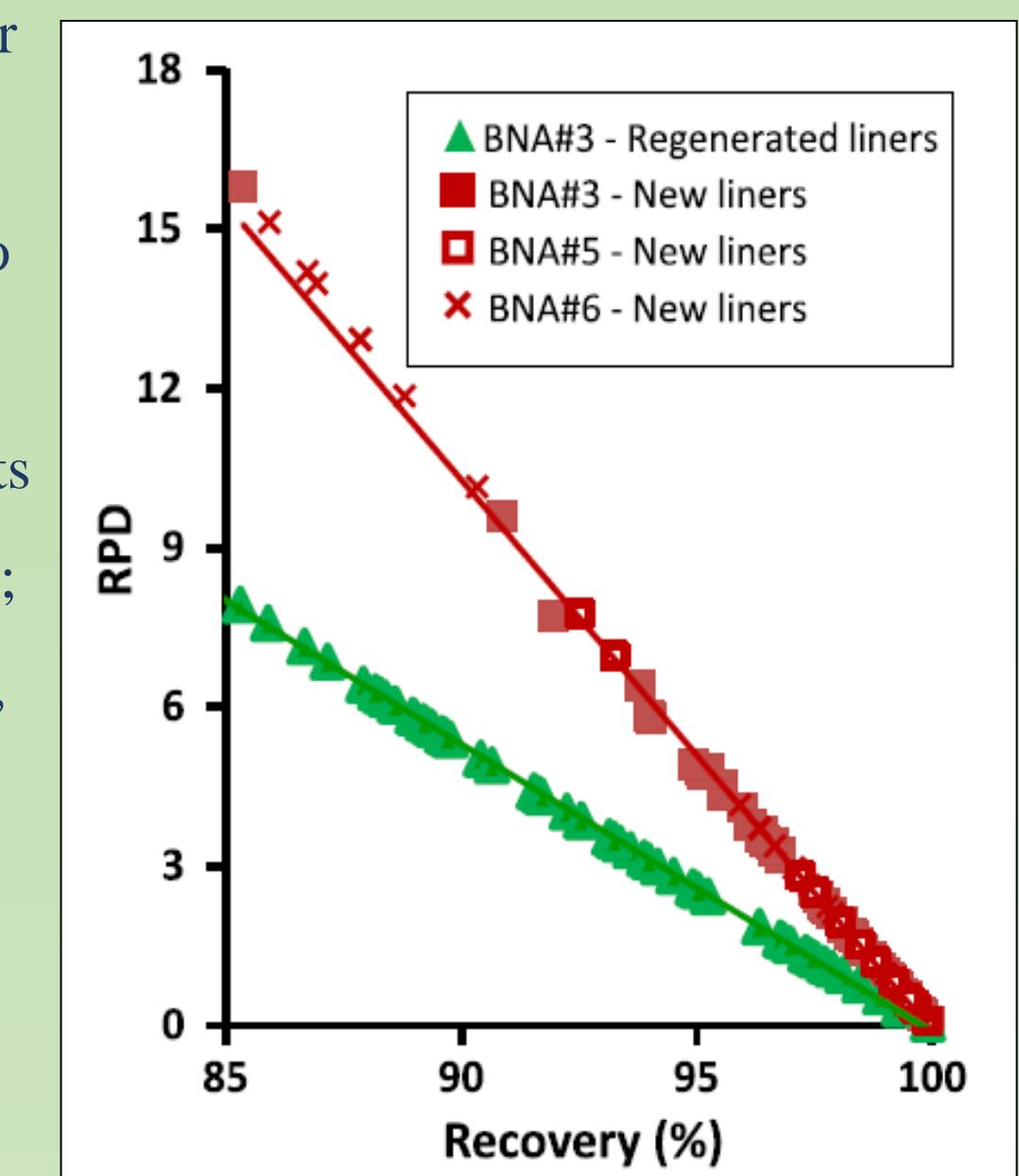
RESULTS

Efficacy of regeneration by percent deviation versus recovery plot – A novel approach for inspecting liner performance is by plotting the RPDs against recoveries (Fig. 1). Strong and unique RPD – % recovery correlation is seen to exist within a particular physicochemical state of a liner set: all the new liners data fell on the same regression line ($\text{RPD} = -1.07[\% \text{ Recovery}] + 107$) irrespective of the GC instruments used. NB: new liners plot has a higher slope than regenerated liners plot implying lesser variance in the precision of measurements using regenerated liners when compared to the new liners.

Data structure and validity – The boxplots of recoveries from samples spiked at 40 and at $80 \text{ }\mu\text{g L}^{-1}$ are shown in Fig. 2. Data from regenerated liners appear to have equal variance at both 40 and $80 \text{ }\mu\text{g L}^{-1}$ spiking levels. On the other hand, data acquired using new liners show unequal variance: the height of the box is smaller at the $40 \text{ }\mu\text{g L}^{-1}$ spiking level and larger at $80 \text{ }\mu\text{g L}^{-1}$.

Three outliers were detected at the $80 \text{ }\mu\text{g L}^{-1}$ spiking level. The boxplots median lines are higher for new liners than for the regenerated liners. In Fig. 2b are the relevant statistics from the boxplots; SDs are small and comparable with each other. Combining this fact with the significant concentrations relation that exist between new liners and regenerated ones at 95% CI ($P < 0.0001$, $n = 61$, not shown), confidence in precision is provided.

Fig. 1 Plots of individual RPD for 61 semi-volatile organic compounds versus % recovery to compare new liners installed in three separate GC-MS instruments (■ BNA#3, □ BNA#5, × BNA#6; regression line: $y = -1.07x + 107$, $R^2 = 0.999$, $n = 183$) with regenerated liners (▲; regression line: $y = -0.541x + 54.0$, $R^2 = 0.999$, $n = 64$). $\text{RPD} = [|SM - AR| / 0.5(SM + AR)] * 100\%$; SM actual amount spiked, AR average recovery of 11 replicate measurements.

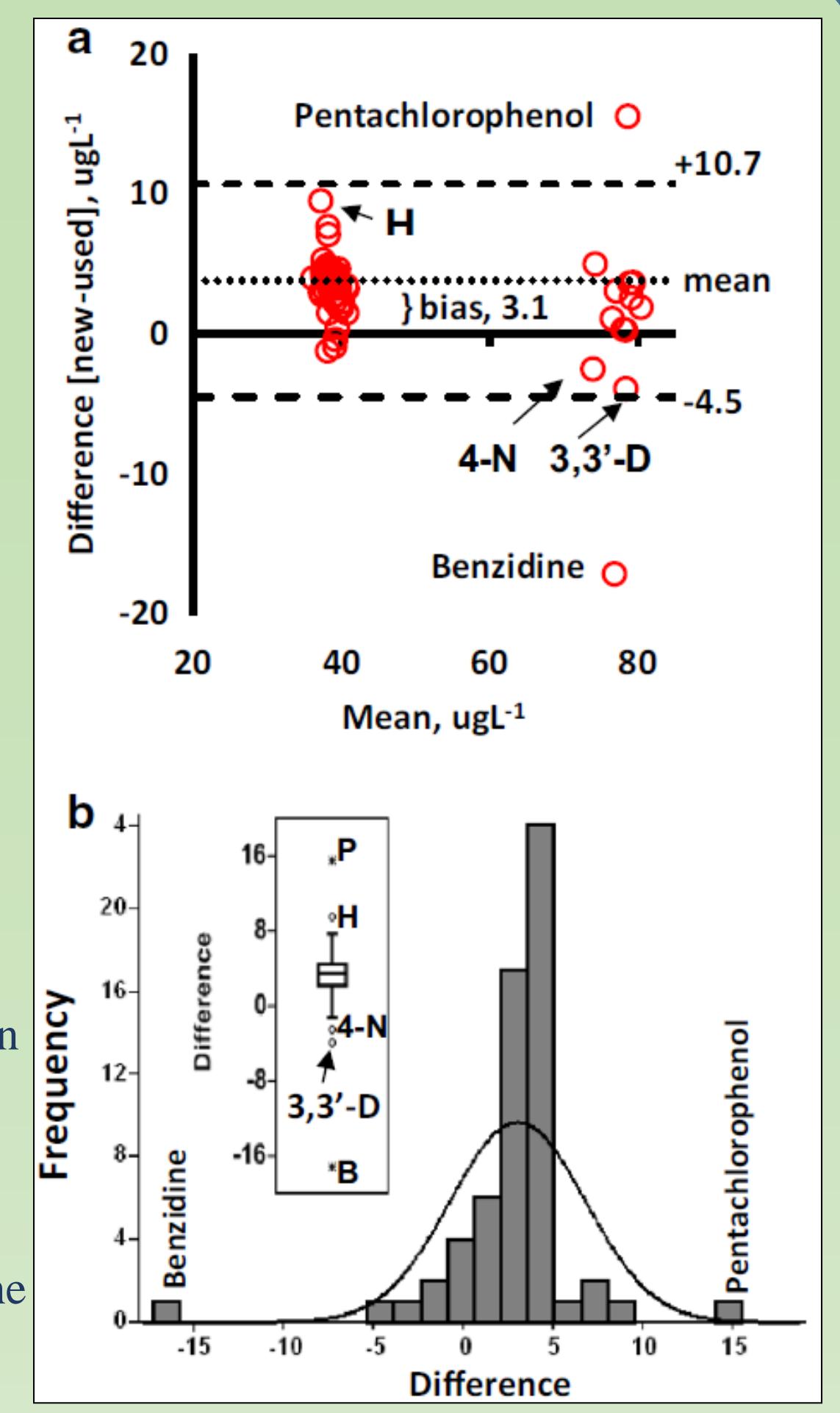


40 $\mu\text{g/L}$		80 $\mu\text{g/L}$		
New	Regen	New	Regen	
mean	40.4	36.8	78.8	77.8
SD	1.1	1.7	4.4	3.7
IQR	1.2	2.2	4.81	2.8
minimum	37.5	32.5	68.3	70.9
Q ₁	39.7	35.4	76.5	77.6
median	40.5	36.9	78.5	78.2
Q ₃	40.9	37.8	81.3	80.4
maximum	42.4	40.0	86.4	85.5

Fig. 2 Boxplot showing the Q_1 , median, and Q_3 for all samples statistics calculated from recovery distributions. **a** Two outliers are shown as ● (benzidine) and ○ (pentachlorophenol). The phenols and benzidines data ($80 \text{ }\mu\text{g L}^{-1}$ spike level, $n = 13$) are skewed below the median (compression above the median). **b** Boxplot statistics showing similar variation in measurements in the new and the regenerated lines.

Fig. 3 shows that regenerated liners can substitute new ones. A $3.1 \text{ }\mu\text{g L}^{-1}$ systematic bias is revealed, but the bias is less than the $\pm 10 \text{ }\mu\text{g L}^{-1}$ limits for measuring SVOCs in industrial wastewater.

Fig. 3 a Bland-Altman plot of the difference recoveries vs mean. H: hexachloropentadiene; P: pentachlorophenol; 4-N: 4-nitrophenol; 3,3'-D: 3,3'-dichlorobenzidine; B: benzidine. A constant bias of $3.1 \text{ }\mu\text{g L}^{-1}$ is observed. **b** Histogram of the distribution of the differences between the paired measurements (bins: 22, start: -17.2 , end: 15.5 ; $n = 59$). The distribution is also shown as a boxplot (inset); the suspected outliers (values falling between $1.5 \times \text{IQR}$ and $3.0 \times \text{IQR}$ outside the IQR corresponding to 3,3'-dichlorobenzidine, 4-nitrophenol, and hexachlorocyclopentadiene from the lowest value to the highest in that order) are plotted with unfilled circle, and outliers (values greater than $3.0 \times \text{IQR}$ outside the IQR representing benzidine at the low end and pentachlorophenol) are plotted with as asterisk. Suspected outliers are one whose values are still within the $\pm 1.96 \text{ SD}$ range



Repeat regeneration – Eleven regenerated liners were put through the entire regeneration process again after the second use to test the potential of repeated liner regeneration. Results show performances similar to those of new liners. No attempt was made to investigate a third round of regeneration.

CONCLUSIONS

This paper provides an opportunity to reduce GC dead time in an environmentally friendly way and cut cost at the same time. The recovery data presented demonstrate that discarded liners can be regenerated through a cycle of sonication, baking and silanization to where their performance meets or exceeds the US EPA Method 625 performance criteria. Currently, there is no freely available method with comparable results.

REFERENCES

Otim O. 2017. Making a case for regenerating GC liners in industrial wastewater screening. Chromatographia, 80(7): 1109-1114. DOI:10.1007/s10337-017-3318-y

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