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LABORATORY SOLVENT REUSE - LIQUID CHROMATOGRAPHY

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Clifford L. Schaffer*

NOVEMBER 1992

Process Development
Waste and Hazard Minimization

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ABSTRACT

The objective of this work was to develop a method for reduction of waste solvent in the Process Engineering Chemistry Laboratory. The liquid chromatographs are the largest generators of explosive-contaminated waste in the laboratory. We developed a successful process for the reuse of solvents from the liquid chromatographs and demonstrated the utility of the process in the assay of hexanitrostilbene.

INTRODUCTION

As part of the Waste Minimization Program in the Explosives Technology Division, we evaluated the solvent usage in the Process Engineering Chemistry Laboratory. The laboratory generated significant amounts of explosive-contaminated waste liquids. The liquid chromatographs (LC) in the laboratory were identified as the major source of the contaminated waste solvents. The most frequent use of the LC was the assay of *sym*-hexanitrostilbene (HNS).

We considered three options for reduction of the contaminated waste solvent. First, the waste solvent could be returned to the solvent feed vessel and reused directly. Second, the waste solvent could be passed through an in-line adsorber such as activated carbon. Third, the waste solvent could be isolated and purified by a process such as distillation prior to reuse. In this report we cover the work on the first two of the three options considered.

RESULTS AND DISCUSSION

Estimates of the generation of explosives-contaminated waste solvent indicates an annual value of about 310 liters. Of this volume approximately 80% arises from the LC operations. The assay of HNS was the single most frequently run LC analysis, and it therefore was the process examined.

A normal-phase LC method for the assay of HNS is presently used. The HNS sample is initially dissolved in acetonitrile to a concentration of 10 mg/40 ml of acetonitrile. All injections are from a 20- μ l loop. Each weighed sample is analyzed four times with a calibration standard run between each injection. The mobile phase flows at a rate of 2 ml/minute and consists of 55% heptane, 30% *n*-butylchloride, and 15% acetonitrile. The mobile-phase feed vessel is a 1-liter flask. The standard run time for a single sample is 15 minutes. This flow generates about 1 liter of waste solvent per 8 hours per chromatograph. Several liquid chromatographs are normally used each workday; they are frequently operated in the automatic mode overnight. The data presented in this report includes the assay for dipicrylethane (DPE), the major impurity found in HNS, and the assay of HNS.

BASELINE SERIES

For the LC solvent to be suitable for reuse, it must not cause the quality of the analysis to suffer. We initially ran a series of LC analysis without solvent reuse on a well-characterized sample to establish a baseline to compare with the solvent reuse results. When the standard method is used, all mobile-phase and injection solvents are considered waste. From one weighed portion of HNS in acetonitrile, seven replicate samples were prepared. The seven replicate samples were used to establish the baseline limits for precision and accuracy. Table I shows the analytical results of the baseline samples. These data show that for a standard HNS assay, a 95% confidence level ($P=0.05$) of 0.53% can be expected. Similarly a precision of 0.30% resulted from the DPE analysis. The spread in the data for the HNS assayed was found to 0.53% and for DPE 0.31%.

We considered three methods for the reuse of the mobile-phase system. Of the three, the least-desirable method was the operation of an external process (such as distillation) before solvent reuse. The demands of providing for distillation made the use of this process undesirable. The two alternative methods are direct solvent reuse without purification and reuse by activated carbon purification of the solvent.

Table I. Assay - No Solvent Reuse					
% HNS	σ	P=0.05	% DPE	σ	P=0.05
98.41	0.16	0.26	1.75	0.14	0.22
98.53	0.28	0.70	1.45	0.15	0.24
98.90	0.34	0.85	1.63	0.24	0.38
98.84	0.14	0.22	1.45	0.14	0.22
98.63	0.08	0.20	1.60	0.21	0.34
98.94	0.36	0.90	1.44	0.23	0.37
98.59	0.37	0.59	1.72	0.14	0.35
Avg. 98.69	0.25	0.53	1.58	0.18	0.30

DIRECT REUSE OF SOLVENT

The simplest solution, although not necessarily the most effective quality-wise, is the reuse of the solvent without purification. The setup used for this experiment was the same as used for the baseline series except the waste stream was directed back to the feed/return vessel, and the feed/return vessel was 100-ml volume instead of the normal 1000 ml. We reduced the volume of the feed vessel in order to amplify by a factor of ten the effect of the unpurified solvent reuse. The injection order was the same as before, but the series of analysis was repeated four times using the untreated recycled solvent. We allowed an additional 8 minutes between injections to permit the baseline of the chromatogram to be re-established.

The data from the four series of runs, listed in Table II, show that the assay values increase only slightly from one set to the next, but the precision decreases dramatically as indicated by the averages of the 95% confidence levels.

SOLVENT REUSE WITH CARBON ADSORPTION COLUMN

The procedure for the third series of assays made use of an activated carbon column in the mobile-phase loop. The column was filled with 4 g of Filtersorb 400 (Calgon). In this series no delay time was required for the chromatograph baseline to stabilize between injections. As with the direct reuse series, the receiver/feed vessel was 100-ml capacity. The data from this series, summarized in Table III, show no loss in precision from one series to the next in contrast to the results in Table II. These data suggest that the carbon column prevented the steady decrease in precision that was shown in the direct reuse of the untreated solvent. A loss of precision with the carbon column series was indicated by comparing the HNS assay's average 95% confidence level of these runs, 1.58%, with that of the baseline series average of 0.53%. The difference is attributed to instrumental effects and/or the addition of the carbon column to the system. We made a second series of runs (Table IV) with the carbon column in place and with a more stable instrument baseline. In contrast to the previous series of runs, the data from the second series show that the carbon column does not cause a precision problem. The 95% confidence levels for the HNS assay, 0.62 and 0.55%, are similar to the 0.53% for the baseline data.

Table II. Assay - Direct Reuse of Solvent					
% HNS	σ	P=0.05	% DPE	σ	P=0.05
Series 1					
98.40	0.25	0.40	1.66	0.05	0.07
98.33	0.80	1.28	1.66	0.04	0.06
98.82	0.42	0.67	1.63	0.04	0.06
98.32	0.45	0.72	1.64	0.03	0.05
98.19	0.08	0.20	1.64	0.02	0.03
98.46	0.09	0.23	1.65	0.03	0.04
98.47	0.12	0.19	1.65	0.04	0.07
Avg. 98.43	0.32	0.53	1.65	0.03	0.05
Series 2					
97.41	1.64	2.62	1.62	0.07	0.11
98.91	0.14	0.35	1.63	0.05	0.08
98.28	1.38	2.20	1.66	0.12	0.19
99.00	0.40	0.64	1.69	0.02	0.03
98.34	1.26	2.02	1.62	0.03	0.05
98.04	1.14	1.83	1.57	0.07	0.11
99.45	0.70	1.12	1.67	0.04	0.06
Avg. 98.49	0.95	1.54	1.64	0.06	0.09
Series 3					
98.52	0.93	1.49	1.69	0.05	0.08
98.87	1.20	1.93	1.74	0.07	0.11
98.28	1.30	2.09	1.70	0.07	0.12
99.20	0.83	1.33	1.64	0.07	0.11
97.64	1.04	1.66	1.63	0.05	0.07
99.16	0.95	1.52	1.63	0.05	0.08
97.97	1.67	2.67	1.64	0.12	0.19
Avg. 98.52	1.13	1.81	1.67	0.07	0.11
Series 4					
98.48	2.17	3.47	1.69	0.05	0.09
97.97	2.09	3.35	1.66	0.01	0.09
99.52	1.62	2.59	1.67	0.04	0.07
98.42	2.30	3.68	1.68	0.12	0.30
98.54	2.01	3.22	1.61	0.07	0.18
98.27	2.05	3.29	1.57	0.10	0.25
99.83	0.56	1.40	1.72	0.02	0.18
Avg. 98.72	1.83	3.00	1.66	0.06	0.16

Table III. Solvent Reuse with Carbon Column

% HNS	σ	P=0.05	% DPE	σ	P=0.05	% HNS	σ	P=0.05	% DPE	σ	P=0.05
Series 1						Series 4					
97.91	0.68	1.09	1.67	0.12	0.19	98.77	0.82	1.32	1.66	0.06	0.10
99.47	0.56	1.41	1.64	0.10	0.16	98.72	1.06	1.69	1.62	0.08	0.12
98.49	0.85	1.36	1.61	0.08	0.13	98.54	0.07	0.18	1.63	0.04	0.06
99.09	1.42	2.28	1.71	0.10	0.15	99.16	0.28	0.70	1.69	0.12	0.19
98.19	0.61	0.98	1.72	0.07	0.11	98.57	0.85	1.36	1.66	0.08	0.13
99.09	0.49	0.79	1.72	0.08	0.13	97.72	1.19	2.98	1.66	0.06	0.16
98.16	1.87	3.00	1.69	0.03	0.05	97.66	0.33	0.53	1.60	0.06	0.10
Avg. 98.63	0.93	1.56	1.68	0.08	0.13	Avg. 98.45	0.66	1.25	1.64	0.07	0.12
Series 2						Series 5					
96.64	2.03	3.25	1.62	0.04	0.07	98.85	1.34	2.14	1.62	0.05	0.09
97.61	0.44	0.70	1.67	0.16	0.26	97.92	0.80	1.28	1.59	0.10	0.16
97.87	0.70	1.13	1.63	0.06	0.09	98.18	0.97	2.42	1.61	0.08	0.13
98.58	0.81	1.29	1.65	0.08	0.13	99.02	0.39	0.62	1.73	0.02	0.04
98.81	0.39	0.62	1.71	0.09	0.15	99.15	0.89	2.23	1.74	0.12	0.19
97.70	0.43	0.68	1.44	0.26	0.42	98.37	1.01	2.52	1.63	0.04	0.09
98.82	0.68	1.10	1.68	0.05	0.08	98.68	1.60	2.56	1.61	0.09	0.14
Avg. 98.00	0.78	1.25	1.63	0.11	0.17	Avg. 98.59	1.00	1.97	1.65	0.07	0.12
Series 3						Series 6					
97.70	0.93	1.49	1.53	0.11	0.18	98.49	0.80	1.28	1.48	0.24	2.18
98.61	0.45	1.13	1.43	0.14	0.22	98.92	0.42	1.05	1.59	0.09	0.22
97.80	1.13	2.81	1.57	0.02	0.04	97.41	0.69	1.72	1.61	0.05	0.09
98.01	1.47	2.35	1.70	0.04	0.07	97.42	0.84	1.35	1.64	0.10	0.16
99.04	0.38	0.61	1.69	0.04	0.06	98.18	1.70	2.73	1.63	0.04	0.07
97.36	1.89	3.03	1.63	0.09	0.14	97.75	0.17	0.27	1.65	0.02	0.18
98.23	1.07	1.71	1.64	0.08	0.13	97.72	1.77	2.84	1.62	0.06	0.10
Avg. 98.11	1.05	1.88	1.60	0.07	0.12	Avg. 97.98	0.91	1.60	1.60	0.09	0.43

Table IV. Solvent Reuse with Carbon Column (Short Series)					
% HNS	σ	P=0.05	% DPE	σ	P=0.05
Series 1					
98.99	0.25	0.40	1.67	0.06	0.10
98.40	0.40	0.64	1.67	0.03	0.05
98.25	0.32	0.51	1.64	0.02	0.03
98.52	0.25	0.63	1.64	0.05	0.08
98.59	0.35	0.89	1.62	0.01	0.02
98.58	0.19	0.47	1.65	0.03	0.05
98.55	0.34	0.84	1.61	0.06	0.10
Avg. 98.56	0.30	0.62	1.64	0.04	0.06
Series 2					
98.50	0.15	0.25	1.63	0.03	0.06
98.66	0.28	0.45	1.67	0.05	0.07
98.71	0.19	0.48	1.59	0.04	0.06
99.05	0.91	1.46	1.65	0.04	0.06
98.63	0.36	0.57	1.69	0.01	0.03
98.74	0.06	0.10	1.67	0.04	0.07
98.60	0.35	0.56	1.64	0.03	0.04
Avg. 98.70	0.33	0.55	1.65	0.03	0.06

CONCLUSION

In today's environmental climate the reduction in solvent usage, even when the quantity is small, is profitable from both the cost savings associated with the purchase of the solvent and even more so from the cost involved with its disposal. The disposal costs are significantly increased when the solvent is contaminated with explosives such as the LC solvents from the laboratory.

The use of in-line carbon columns to remove traces of explosive contaminants from LC solvents is inexpensive, easy to install, and yields high-quality analytical results. As the data show, a series of HNS samples and calibration standards involving 336 chromatographic injections can yield quality results with no observable degradation to the solvent system. The use of an in-line carbon column should be applicable to other LC analyses involving other explosives as well as to a variety of other non-explosive materials.

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