American Society of
Agricultural and Biological Engineers

A Novel Approach to CAFO Odor Assessment: Odorant Field Collection by Sorbent Tube / Thermal Reconstitution in the Laboratory

DONALD W. WRIGHT, David K. Eaton, Lawrence T. Nielsen, Fred W. Kuhrt;
Microanalytics (a MOCON Company), Round Rock TX; Jacek A. Koziel, Lingshuang
Cai, Yin-Cheung Lo (Agricultural & Biosystems Engineering Dept, Iowa State
University), Ames, Iowa; David B. Parker, Zena Perschbacher-Buser (West Texas A&M
University), Canyon, Texas

ABSTRACT

Historically, odor emission monitoring of high density livestock operations has been
limited to direct, whole-air assessment utilizing remote site sampling by plastic bags,
human sensory panelists and dynamic dilution olfactometry. On-going efforts by these
authors are directed at enabling the translation of these sensory 'only' monitoring
protocols to instrument 'primarily, with sensory oversight' alternatives. This current work
attempts to address the latter requirement for sensory oversight and the associated need
for improved methods of remote site whole-air sample collection. Published works by
these authors as well as others places in serious question the appropriateness of the use of
plastic bags for the challenge of CAFO odor assessment; especially relative to sample
points at increasing downwind distance from the source. Concerns increase due to the
associated natural dilution effects relative to priority semi-volatile odorants. This current
submission reports on the progress to date in the development and evaluation of
alternative whole-air sampling strategies which attempt to address the primary limitation
of plastic sampling bags; the adsorption loss-to-wall of high impact semi-volatile
odorants such as p-cresol. In this approach the actual field air sampling is carried out
utilizing sorbent tubes for on-site collection of the volatiles/odorants from a measured
volume of air. These sorbent tube collections are then transported to the laboratory for
reconstitution within a heat traced, passivated and piston-displaced vessel prior to
composite odor assessment. The sample reconstitution process is accomplished simply by

1

thermally desorbing the collected odorants into a flowing diluent gas stream and making up to final volume to yield a match of the originally sampled environment.

Keywords: malodor analysis, agricultural odor analysis, farm odor, GC-Olfactometry, GC-O, solid phase microextraction, SPME, multidimensional gas chromatography, livestock housing

INTRODUCTION

In recent years, hundreds of potential odorants have been reported in the literature for CAFO odor emission sources (Schiffman at al. 2001; Oehrl et al. 2001; Willers et al., 2003; Mosier et al., 1973; McGinn et al., 2003; Keener et al., 2002; Hutchison et al., 1982; Zahn et al., 2001). However, recent work by these authors (Wright et al., 2005; Cai et al., 2006; Koziel et al., 2006) suggests that from this very large suite of potential odor contributors, distant downwind community odor complaints may be largely driven by a relatively small subset of odorants drawn from this very large field. More importantly, perhaps, is the fact that this small subset of prioritized odorants appears to be dominated by semi-volatile compounds characterized by extreme odor potency and low volatility. In recently reported results for example (Wright et al., 2006), the authors demonstrated that a synthetic formulation composed of only five prioritized odorants represented a generally recognizable 'barnyard downwind' odor character match. In this case, the five prioritized odorants were butyric acid, isovaleric acid, p-cresol, 4-ethyl phenol and 2-amino acetophenone. The latter three compounds are clearly drawn from the semi-volatile category and invoke the associated constraints regarding sampling and analytical strategies. Of the three semivolatiles, p-cresol appears to warrant particular consideration due to indications that its odor impact may approach 'character defining' status under some operational and environmental conditions. This odor impact dominance in conjunction with the well documented propensity for adsorption driven loss to the walls of plastic sample containers drives the need for improved sampling alternatives to the widely utilized plastic gas sampling bags.

Reported herein are results, to date, toward establishing feasibility of a specially passivated, heat traced, positive displacement stainless steel cylinder as an improved whole-air sampling vessel. These results suggest that such an approach should enable improved recovery of the range of odorants represented in the CAFO application, including the high impact and problematic semi-volatile compounds. In addition, also reported are results of initial efforts to integrate this alternative whole-air sample vessel into an effective sampling strategy which is optimized with respect to the CAFO downwind odor application. Based upon these initial results the integrated sampling strategy appearing to hold the greatest promise is an indirect approach. This indirect approach involves initial CAFO downwind odorant sampling utilizing sorbent tube collection followed by at-instrument thermal desorption and reconstitution to the 'original' whole-air form. These results report on the progress-to-date relative to prototype hardware development and evaluation. Although initial p-cresol recovery efficiencies are well below targeted goals, an excellent experimental format has been

developed and is expected to enable a continued incremental improvement with respect to design and target odorant recoveries.

MATERIALS and METHODS

Whole-air Sampling Cylinder Prototype:
The primary objective of this project is to explore the feasibility of a specially passivated, heat traced, positive displacement stainless steel cylinder for whole-air sampling. To expedite the feasibility study, prototype development was centered around a commercially available moving piston cylinder from Welker Engineering of Sugarland, Texas. The basic 1000 ml, 316 stainless steel sampling cylinder was modified for the application by SilcoSteel passivation and the addition of an extension rod and handle for manual operation. Heat tracing of the cylinder was provided by a custom thermocouple feedback controlled flexible heating mantle from Glass-Col of Terre Haute, Indiana. For purpose of this feasibility project filling and delivery of the gas samples was by manual, syringe action control.

Whole-air Sampling Bag Prototype:
As a result of initial disappointing recovery results with the SilcoSteel based passivation choice, additional comparative p-cresol recovery work was carried out utilizing standard and custom made specialty film sampling bags. Two types of bags were utilized during this work. The first of these was based on an Inconel / Silver metalized FEP specialty film from the aerospace industry. The second sampling bag type was a commercially available Tedlar bag manufactured by SKC of Eighty Four, PA. The latter was obtained in a standard 1000 ml form but was modified by resealing to produce the required 500 ml volume match to the in-house fabricated, metalized FEP equivalent. Teflon access port valves were incorporated into both bag types for the comparative p-cresol recovery runs. Heat tracing of the sampling bags was provided by a thermocouple feedback controlled flexible heating chamber from Restek Corporation of Bellefonte, PA. For purpose of this feasibility project, filling and delivery of the gas samples was by way of an in-house fabricated vacuum / pressurization chamber.

SPME Sampling:
Solid phase microextraction (i.e. SPME) (Cai et al., 2006; Koziel and Novak, 2002; Koziel and Pawliszyn, 2001; Chai and Pawliszyn, 1998, Chai and Tang, 1998) utilizing a 1 cm Carboxen modified PDMS - 85 μm fiber was the headspace sampling technique applied for the required p-cresol recovery analyses. SPME collections were carried out under various conditions of collection during the study; @ 50 deg C at the calibrant generator exit port; 50 deg C within the sample cylinder and @ 22 deg C (room temperature) at the unheated external PTFE sampling port.

Multidimensional Gas Chromatography-Mass Spectrometry:
MDGC-MS is an integrated approach combining multidimensional GC separation techniques with conventional GCMS instrumentation. A commercial integrated AromaTrax™ system from Microanalytics (a MOCON Company) of Round Rock, Texas was used for the MDGC-MS work in support of the p-cresol recovery data presented

below. Details regarding hardware and operational parameters have been described in detail in past publications (Wright et al., 2005; Cai et al. 2006) and are not restated here.

p-Cresol Trace Calibration Gas Generator:
Development of a p-cresol calibration / challenge gas generator was undertaken in parallel with the design and construction phase of the prototype sampling cylinder. The goal was a permeation based calibrant generator which could yield long-term, precise delivery of trace level of p-cresol for use in optimization of the proposed alternative device. It was also required for proposed cross-comparison studies to be carried out relative to plastic bags, Summa canisters or other conventional, whole-air sampler devices. The calibrant generator was based upon a certified p-cresol emitter tube and dilution chamber from Kin-Tek Corporation of LaMarque, Texas. Integrating this assembly with a gas chromatographic forced air oven for temperature control and constant pressure / fixed restriction control of downstream calibrant dilution resulted in an integrated system producing a high degree of short-term and long-term precision.

RESULTS and DISCUSSION

Past MDGC-MS-O odor profile and synthetic odor matching efforts by these authors have indicated that a relatively small number of semi-volatile odorants may carry a major proportion of odor impact with respect to swine and cattle CAFO downwind. As a result of its apparent 'character defining' downwind odor impact and a high propensity for adsorption onto contact surfaces, p-cresol, one of many semi-volatile emissions from these sources, is believed deserving of particular focus. Therefore, for purpose of this study, a decision was made to focus on trace level, gas phase p-cresol as the single representative challenge odorant. The rationale behind this decision was that it would simplify and expedite the exploratory recovery study by focusing on, what may be, the single most important odorant emission from swine and cattle CAFO sources. In addition, it was felt that the same factors determined to be critical for optimized p-cresol recovery would prove to be applicable to the other high impact semi-volatile odorants as well.

Development of a p-cresol calibration / challenge gas generator was undertaken in parallel with the design and construction phase of the prototype sampling cylinder. As shown in Table 1 below the in-house odorant challenge gas generator was able to produce a high degree of both short-term and long-term precision.

Table 1
p-Cresol Calibration Gas Generator - Short Term / Long Term Precision

Parameter	Short Term	Extended Term	Long Term
time span	1 day	2 day	1 week
mean	3,492,628	3,731,614	3,569,426
sd	88,540	294,550	183,663
% RSD	2.54%	7.89%	5.15%

n	5	11	3
constraint	sequential	sequential	sequential

As shown in the above table, five sequential runs of a 3 ppb standard at 50 degrees C for a 30 minute collection time resulted in a precision level of 2.54% RSD. Multi-day calibration check series resulted in corresponding long-term precision results of less than 8% RSD. This level of precision was felt to be adequate to track recovery optimization progress with respect to the proposed alternative whole-air sampler devices (i.e. inertized cylinder, specialty sampling bags or others).

As early recovery results in Table 2 below indicate, our initial selection of SilcoSteel passivation for surface activity reduction with respect to p-cresol was clearly incorrect. Although this commercial passivation treatment is promoted as imparting reduced adsorption activity, supporting data has primarily been developed relative to lower molecular weight sulfur and halogenated species. Clearly, based upon the data below, this surface activity reduction does not translate to the target compound of current focus, p-cresol.

Table 2
p-Cresol Comparative Recoveries – Sample Contact Surface Adsorption Activities

Material	Conditions	Response (avg of 2)	% Recovery*
SilcoSteel Passivated	1/16 in X .030 ID	10,618	0.3
Glass Lined SS Heated	1/16 in X .8 mm ID	74,378	2.1
PTFE Thinwall Unheated	1/16 in X .9 mm ID	369,615	10.4
* Recoveries referenced back to previous p-cresol calibrant output results (i.e. 3,569,426 at the gas generator exit sampling port heated to 50 deg C).

It is likely, although unproven at this point, that similar poor recovery results will be shown for other compounds drawn from the category of polar semi-volatiles. Although somewhat improved, similar low recovery results were shown relative to the heat-traced glass lined stainless steel (i.e. GLT) transfer line. In comparison to the first two surface types however, PTFE appeared to represent a relatively dramatic improvement. In spite of being unheated, the PTFE transfer resulted in an immediate @ 35X increased p-cresol recovery relative to SilcoSteel and an @ 5X increased recovery relative to heat-traced GLT. In retrospect, the p-cresol recovery enhancement shown for PTFE is consistent with the previous data reported by these authors with respect to FEP gas sampling bags (Koziel et al 2005). Unfortunately, due to the expense of the cylinder and Teflon passivation process it was not possible, within the budget of the current study, to replace the SilcoSteel passivated Welker cylinder with a PTFE clad equivalent. As a result, an

attempt was made to press forward with the available hardware to explore the other basic design and experimental concepts.

Utilizing the initial experimental format, the next series of experiments focused on the concept of whole-air thermal reconstitution from sorbent tube collection. In this series, summarized in Table 3 below, an indirect approach was taken to whole-air assessment. In this case, a measured volume of the p-cresol calibrant gas was pulled through a prepared sorbent bed (i.e. 60/80 Chromosorb 102 packed GLT tube); concentrating the p-cresol odorant on the sorbent bed and venting the resulting 'purified' air matrix. The sorbent tube with adsorbed p-cresol was then physically transferred to the thermal desorption device attached to the reconstitution cylinder. This was immediately followed by thermal desorption of the p-cresol from the sorbent bed @ 250 deg C into the nitrogen sweep gas and into the cylinder for reconstitution to the desired final volume (i.e. purified room air as diluent). Although not exhibiting maximum p-cresol recovery, as shown in the experimental results that follow the process resulted in initial validation of the concept sequence (1) sorbent tube collection (2) thermal reconstitution (3) whole-air assessment.

Table 3
p-Cresol Comparative Recoveries – Reconstitution from Sorbent Collection Series

Collection Matrix	Conditions	Response	% Recovery*
1 hr post reconstitute Chromosorb 102 in 1/8 in GLT Sorbent Tube	900 ml calibrant gas @ room temp drawn from calibrant exit port @ 50 deg C – reconstituted to 1000 ml @ 50 deg cylinder	306,534	7.8
Recheck – 2 hr post reconstitute		257,559	6.6
Recheck – 3 hr post reconstitute		203,057	5.2
*Recoveries referenced back to same day p-cresol calibrant output results (i.e. 3,930,751 average of 6 bracketing runs @ 6.4% RSD - at the gas generator exit sampling port heated to 50 deg C).			

These results illustrate two important considerations relative to the current study. Firstly, at the @ 8 % level, p-cresol recovery for the initially reconstituted whole-air sample approaches the @ 10% level which was achieved for PTFE direct transfer in the previous transfer line recovery series. Even though this level of recovery is far below that targeted, it is significant that the indirect, sorbent tube collect / thermal reconstitute approach did not appear to result in dramatic additional p-cresol losses (i.e. @ 25% additional loss). Key considerations include: (1) the reference PTFE line transfer recoveries were

structured such that all sample contact surfaces from calibrant exit to cylinder interior were PTFE only; (2) the initial sorbent tube was constructed from GLT which, based upon the previous data, is a contact surface material clearly inferior to PTFE relative to p-cresol recovery and (3) the thermal desorption process resulted in gas phase contact of p-cresol with the GLT surface of the sorbent tube as well as the Silcosteel passivated surfaces of the machined cylinder transfer pathways. It is likely that the recovery differential will be eliminated or significantly reduced as the indicated design optimization efforts are applied (i.e. (1) PTFE lining of sorbent trap tubes, interface hardware components and cylinder internal contact surfaces and (2) surface heat-tracing design optimization).

The second major consideration which can be taken from this series is the dynamic nature of the loss-to-wall effect. This is illustrated by the additional @ 33% loss of p-cresol upon extended equilibration for 3 hours post-reconstitution. Taking into consideration the competitive loss due to the 2 preceding SPME sample collections and the length of the post-reconstitution standby (i.e. 3 hours) this rate of loss may not be excessive; especially in relation to the dramatic losses encountered initially (i.e. at the time of transfer to the cylinder). It appears that much of this dramatic initial p-cresol loss results from the high level of activity of the SilcoSteel passivated surface. It is possible, although unproven at this point, that the dynamic loss-to-wall rate will be reduced as the above indicated surface and design modifications are applied.

Although the calibrant / challenge gas generator had proven the ability to produce excellent run to run repeatability, the long-term experience demonstrated that excursions were possible as a result of operational temperature swings brought about by extreme weather events.

Table 4
p-Cresol Calibration Gas Generator –
Effect of Outside Temperature Swing*

Run Number	Response
1	1,610,571
2	1,671,842
3	2,047,828
mean	1,776,747
sd	236,753
% RSD	13.3%
n	3
*Resulting from an unusual cold weather event (i.e. 2-3 days in the 20 to 33 deg F range). Previous reference data generated during more typical 75 to 90 deg F range.	

The series summarized in Table 4 above exhibited p-cresol responses which were @ 50% lower than expected, based upon the previous data which was accumulated over several weeks. The p-cresol response drop appeared to correspond to an unusual weather event; dramatically lower than normal temperatures which were sustained over an unusually long period of time. This dramatic drop in response occurred in spite of efforts to maintain all instrument and environment parameters identical to those used for previous data collections. It appears that this excursion resulted from the temperature effects on the instrument air generator compressor which was located in an unheated warehouse location. It is assumed, but unproven at this point, that pre-cooling of the air feed to the calibrant generator was sufficient to cause this shift in the p-cresol output. Based upon this indication, plans were made to install a temperature preconditioning heat exchanger upstream of the calibrant gas generator. In advance of this modification all follow-on experiments were referenced to bracketing calibration analyses performed the day of a targeted experimental series.

The results summarized in Table 5 below appear to suggest that an enhanced recovery of p-cresol can be realized if the adsorbent loaded portion of the SPME fiber is inserted deeper into the reconstitution cylinder. In this case the stand-off height of the SPME fiber access port assembly was reduced by reconfiguring. This resulted in an increase in the insertion depth of the fiber tip from 12 mm to 50 mm; distances which, in effect, represent the separation distance from the wall. The @ 16% higher p-cresol recoveries for the deeper fiber insertions appears to suggest that the unmixed contents of the cylinder are significantly impacted by 'wall effects'. In this case the wall effect appears to be a stratified, diminished p-cresol concentration zone nearest the highly active SilcoSteel cylinder wall surface; resulting in lower p-cresol yields for samples collected within that diminished concentration zone. This effect, if verified, serves as added evidence of the unacceptable activity level of SilcoSteel with respect to p-cresol. The levels of p-cresol response in this series represent the maximum which were achieved utilizing the SilcoSteel passivated cylinder and referencing back to the p-cresol concentration level as sampled at the 50 deg C heated exit port of the calibrant generator.

Table 5
p-Cresol Comparative Recoveries – Dynamic Loss to Wall Effect - Repeatability

Experiment	Conditions	Response	% Recovery*
Shallow Insertion Reference	@ 12 mm	397,617	17.4
Deep Insertion #1 – Day 2 recharge post overnight purge	50 mm	764,647	19.0
Deep Insertion #2 – Day 2 recharge without interim purge	50 mm	834,366	21.0
Deep Insertion #3 – Day 5 recharge post overnight purge	50 mm	800,421	20.6

* Referenced back to same day p-cresol calibrant output results (i.e. shallow insertion referenced back to 2,282,332 average of 2 runs collected at the exit sampling port heated to 50 deg C; Day 2; 3,973,170 average of 2 runs collected at the exit sampling port heated to 50 deg C Day 5; 3,883,608 average of 2 runs collected at the exit sampling port heated to 50 deg C).

At this point in the project the experimental format was changed to correct for the immediate (i.e. and relatively dramatic) drop of p-cresol concentration upon exiting the heated zone of the calibration gas generator. An alternate experimental format was set-up to evaluate the effect of collecting downstream from the heated exit sampling port. This alternate format utilized an unheated external sampling port constructed of PTFE. In this case both the calibration gas charge to the cylinder and the cylinder discharge gas are collected from this same port, utilizing the same PTFE transfer tube. The rationale behind this strategy was that this would bring the cylinder recovery response values in closer correspondence relative to the actual cylinder loading concentrations. Simply stated, utilizing the same sample point and same transfer line under the same conditions, any drop in p-cresol loading should be the result of losses suffered upon contact with the active surface of the reconstitution vessel being evaluated. The p-cresol recovery precision series summarized in Table 6 below was generated to determine the level of short-term precision which is achievable for this unheated external PTFE sampling port.

Table 6
p-Cresol Response Short Term Precision –
Unheated External PTFE Sample Port

Run Number	Response
time span	1 day
mean	1,854,185
sd	102,395
% RSD	5.52%
n	4
constraint	sequential

This series confirmed that, in spite of being unheated, the external sample port yielded good precision relative to the p-cresol challenge. This level of precision was found to be consistent with the corresponding precision data generated previously for the heated calibrant generator exit port @ 50 deg C. Considered in relation to the previous heated exit port loading levels, this data further confirms the rapid and relatively dramatic drop in p-cresol concentration in the short length of unheated PTFE transfer line.

The results in Table 7 below demonstrated that there is a significant boost in apparent recovery values realized as a result of the action to 'correct' the reference vessel charge concentration levels (i.e. to more closely reflect the actual p-cresol loading in the final

challenge gas feed to the vessel). It also further demonstrates the sampling challenge associated with p-cresol in particular and polar semi-volatiles in general. In spite of the very short 30 cm length and small 8.5 sq cm contact surface area of the PTFE transfer line there is a relatively dramatic and immediate loss of this critical odorant to the walls of the transfer line. All subsequent experimental p-cresol recovery results were referenced to the 'corrected' p-cresol loading values developed for the external, unheated, PTFE sampling port.

The rationale behind the use of the same transfer line and sample point for calibrant gas influent (i.e. p-cresol challenge) and cylinder effluent (i.e. p-cresol recovery) is that this approach has the best chance of taking all factors out of the equation with the exception of the p-cresol loss-to-cylinder wall. The down side to this approach is the background carryover between runs but, for purpose of this study, this factor is assumed to be constant.

Table 7
p-Cresol Comparative Recoveries – 'Corrected' Loading Levels (PTFE Unheated External Sampling Port)

Experiment	Experimental Test Parameters	% Recovery
p-cresol recovery - cylinder	Temperature effect; 50 deg C	47
p-cresol recovery - cylinder	Temperature effect; 75 deg C	51
p-cresol recovery - cylinder	Temperature effect; 100 deg C	50
p-cresol recovery – FEP* bag	FEP vs. Tedlar™; 75 deg C	66
p-cresol recovery – Tedlar™ bag**	FEP vs. Tedlar™; 75 deg C	25
p-cresol recovery – FEP* bag	Temperature effect; 23 deg C	86
p-cresol recovery – FEP* bag	Temperature effect; 75 deg C	68
p-cresol recovery – FEP* bag from sorbent delivery	Sorbent delivery; 23 deg C from Chromosorb 102 collection	60
* - metalized FEP ** - commercial Tedlar (modified)		

The first recovery series summarized in Table 7 above (i.e. runs #1 through #3) were carried out as an initial test of the effect of increasing cylinder temperature on p-cresol recovery. Whereas the first and all previous p-cresol recovery data was generated utilizing a 50 deg C cylinder temperature the latter two runs were carried out at 75 deg C and 100 deg C respectively. The second run of this series did appear to indicate a modest (i.e. @ 9%) incremental increase in p-cresol recovery in response to the 25 deg C

increase in cylinder temperature. However, the third run of the series appeared to contradict these conclusions. The increased cylinder temperature (i.e. 100 deg C) failed to produce the expected boost in p-cresol recovery relative to the 75 deg C equivalent. It is unclear, at this point, whether this contradiction results from a 'diminishing returns' effect relative to the clearly active SilcoSteel surface or some other factor. Other factors might include, for example, carryover temperature increase effects from the cylinder effluent. Such carryover temperature increase effects could result in corresponding thermal expansion effects and competing adsorption efficiency effects acting on the SPME collection process. Regardless, a decision was made, at this point, to abandon any additional comparative p-cresol recovery work with the SilcoSteel passivated cylinder and switch to a clearly superior (i.e. relative to p-cresol) FEP based alternative. As with previous recovery series, this last experimental set did serve to further confirm the run to run repeatability of the experimental format (i.e. 1,744,795 and 1,772,021 count for sequential calibrant runs and 49.3% and 49.8% yield for the corresponding sequential p-cresol recovery runs).

From the results summarized above, Teflon (i.e. PTFE or FEP) appears to be the superior surface treatment for the proposed heat traced sampling concept. Unfortunately, as a result of the prohibitive cost of replacing the original SilcoSteel passivated Welker cylinder with a preferred PTFE or FEP clad equivalent, a less costly approach was sought to further explore concept feasibility. An interesting alternative was enabled through the discovery of an obscure source of a specialized film from the aerospace industry; metalized, heat wieldable FEP films utilized in insulation blankets and mirror surfaces. In theory this material presents us with the opportunity to fabricate inexpensive gas bag samplers reflecting the two targeted requirements which are the basis of this study; (1) a demonstrated superior Teflon surface treatment to minimize surface adsorption activity relative to p-cresol and (2) a metalized outer cladding to enable heat tracing of the container to further enhance p-cresol recoveries (i.e. while minimizing the possibility of competing p-cresol loss due to accelerated through-wall permeation). The final p-cresol recovery series, summarized in Tables 7 above, were carried out to evaluate this new metalized film material as a possible improved alternative to Tedlar. In this case, p-cresol recovery assessments were carried out under identical conditions for in-house fabricated metalized FEP bags and in-house modified commercial Tedlar equivalents.

These results act as further confirmation of the superiority of the FEP film surface in comparison to Tedlar with respect to p-cresol recovery. They are consistent with previously published study results (Koziel et al 2005) as well as those of the current study which are summarized in the preceding paragraphs. Upon direct comparison, the @ 66% average p-cresol recovery value for the metalized FEP bag is significantly better than the @ 25 % shown for the Tedlar equivalent. The 66% value from the current study is believed to be particularly significant considering the small size of the comparative sample bags (i.e. 500 ml in comparison to the 10 liter size of the bags utilized in the previously published study results). Although the current p-cresol recovery values are very close to the previously published values (i.e. @ 67%) it is significant that, if the higher ratio of wall surface to internal volume of the smaller bags is taken into account (i.e. @ .36 to @ .71, representing an @ 97% ratio increase), the smaller bags would have

been expected to see an increase in the rate of loss to the wall, all other factors being equal.). Similar results were shown for the comparative recovery runs carried out with the commercial Tedlar equivalent (i.e. 1 liter volume modified by resealing one edge to yield the targeted 500 ml volume equivalent of the metalized FEP bags). The average p-cresol recovery values of 25% are slightly higher than the 16% values reported in the previous study results. ***It was initially felt that the lower than expected loss shown for the smaller bag resulted from the heat tracing of the container during the current work (i.e. 75 deg C in comparison to room temperature for the previous study). In fact, results from a subsequent isolated experimental procedure, place into question this conclusion. As shown in Table 7 above a single recovery experiment carried out with a new FEP bag @ room temperature resulted in the highest p-cresol recovery values realized to date, (i.e. 86%). Although there is not sufficient data to confirm an increased rate of loss with increasing temperature effect it appears to be sufficiently consistent to warrant further investigation. Additional experimental work will be required to clarify these apparent inconsistencies relative to increasing temperature and p-cresol recovery effects.***

CONCLUSIONS

A number of conclusions can be drawn from the results summarized in the preceding sections. These include the following, arranged in approximate order of descending priority:

- FEP or PTFE appears to be far superior to SilcoSteel for reducing surface activity relative to trace level, gas phase p-cresol.
- Neither Silcosteel passivation nor the borosilicate glass surface of GLT appears to be appropriate for trace level, gas phase p-cresol.
- Based upon p-cresol recovery results alone, the proposed concept of whole-air odor assessment through sorbent tube collection and thermal reconstitution does appear to be feasible.
- All other parameters being equal, increasing the contact surface temperature of the sampling chamber results in an incremental increase in the yield of p-cresol.
- In spite of a demonstrated inferior p-cresol recovery performance relative to Teflon, the heat traced SilcoSteel passivated cylinder appears to yield superior p-cresol recovery levels relative to Tedlar. However, as a result of differences in volume and surface to volume ratios between the two devices, these results must be interpreted as tentative until confirmed under equivalent conditions.
- To maximize long-term precision of permeation tube based semi-volatile calibrant generators it is necessary to precondition to temperature, the diluent gas feed to the dilution chamber.

On-going efforts are directed at establishing a better understanding of the ***relationships between vessel surface treatment, vessel temperature strategy and p-cresol recovery***. These findings are expected to enable the optimization of the alternative whole-air sampling device and strategy. Based upon the results to date, key design considerations include: 1) heat traced stainless steel cylinder; 2) PTFE or FEP wetted surface cladding of cylinder interior; 3) thin film Teflon surface cladding to minimize potential 'reservoir'

loss volume; 4) Teflon lined stainless steel sorbent tubes; 5) minimal time delay between reconstitution process and whole-air assessment.

ACKNOWLEDGEMENTS

REFERENCES

Cai L., J.A. Koziel. Y.C. Lo, and S.J. Hoff. 2006. Characterization of VOCs and Odorants Associated with Swine Barn Particulate Matter using SPME and Gas Chromatography-Mass Spectrometry-Olfactometry. Journal of Chromatography A, 1102 (1-2), 60-72

Chai, M. & Pawliszyn, J. 1995: Analysis of environmental air samples by solid phase microextraction and gas chromatography / ion trap mass spectrometry. Environmental Science and Technology. Vol 29 (3), (1995).

Chai, M. & Tang, Y. 1998: Solid phase microextraction (SPME) analysis of whole air samples. Journal of Environmental and Analytical Chemistry. Vol 72 (1), pp 77-82, (1998).

Hutchinson, G.L.; Mosier, A.R. & Andre, C.E. 1982: Ammonia and amine emissions from a large cattle feedlot. Journal of Environmental Quality. Vol 11 (2), (1982).

Keener, K.M.; Zhang, J.; Bottcher, R.W. & Munilla, R.D. 2002: Evaluation of thermal desorption for the measurement of artificial swine odorants in the vapor phase. Transactions of the ASAE. Vol 45 (5), pp 1579-1584, (2002).

Koziel, J.A., L. Cai, D. Wright, S. Hoff. 2006. Solid phase microextraction as a novel air sampling technology for improved, GC-Olfactometry-based, assessment of livestock odors. *Journal of Chromatography Science*, July issue, in press.

Koziel J.A., Spinhirne J.P., Lloyd J.D., Parker D.B., Wright D.W., and Kuhrt F.W. Evaluation of sample recovery of malodorous gases from air sampling bags, SPME and sampling canisters. *J Air Waste Manage. Assoc*. 55: 1147-1157 (2005).

Koziel and J. Pawliszyn. Air sampling and analysis of VOCs with solid phase microextraction. Journal *of the Air & Waste Management Association*. 51:173-184 (2001).

Koziel, J.A., I. Novak. Sampling and sample preparation strategies based on solid phase microextraction for analysis of indoor air. *Trends in Analytical Chemistry*. 21: 840-850 (2002).

McGinn, S.M.; Jantzen, H.H. & Coates, T. 2003: Atmospheric ammonia, volatile fatty acids and other odorants near beef feedlots. Journal of Environmental Quality. Vol 32, pp 1173-1182, (2003).Mosier, A.R.; Andre, C.E. & Viets F.G. Jr. 1973: Identification of aliphatic amines volatilized from cattle feedyard. Environmental Science and Technology. Vol 7 (7). (1973).

MSDS 2002: CAS number 7783-06-4 . Aldrich Chemical Company, Inc., Milwaukee, Wi., USA. Valid period 11/2001 to 01/2002.

Oehrl, L.L; Keener, R.W.; Bottcher, R.D.; Munilla, R.D. & Connely, K.M. 2001: Characterization of odor components from swine housing dust using gas chromatography. Applied Engineering in Agriculture. Vol 17 (5), pp 659-661, (2001).

Schiffman, S.S., J.L. Bennett, J.H. Raymer. Quantification of odors and odorants from swine operations in North Carolina. Agricult. Forest Meteorol. 108: 213 – 240 (2001).

Willers, H.C.; Hobbs, P.J. & Ogink, N.W.M. 2003: Odors from evaporation of acidified pig urine. Proceedings of the 3rd International Conference, Research Triangle Park, NC, October 2003.

Wright, D.W.; Mahler, K.O. & Ballard, L.B. 1986: The application of an expanded multidimensional GC system to complex fragrance evaluations. Journal of Chromatographic Science. Vol 24, pp 60-65, (1986).

Wright, D.W. 1997: Application of multidimensional gas chromatography techniques to aroma analysis. In: Techniques for Analyzing Food Aroma (Ray Marsili, ed.). Marcel Dekker, Inc., NY, (1997).

Wright, D., L. Nielsen, D. Eaton, F. Kuhrt, J.A. Koziel, J.P. Spinhirne, D.B. Parker. 2005. Multidimensional GC-MS-olfactometry for identification and prioritization of malodors from confined animal feeding operations. Journal of Agricultural and Food Chemistry, 53(22), 8663-8672.

Wright, D., L. Nielsen, D. Eaton, F. Kuhrt, J.A. Koziel, J.P. Spinhirne, D.B. Parker. 2006. Synthetic CAFO odor formulation; an effective technique for validation of odorant prioritizations;. Accepted for presentation at Workshop on Agricultural Air Quality: State of the Science,; Potomac, Maryland, June 2006

USEPA Website (2003): Odor characterization, assessment and sampling. In: Guide to Field Storage of Biosolids – Appendix A. www.epa.gov, (July, 2003).

Zahn J.A.; DiSpirito A.A.; Do Y.S.; Brooks B.E.; Cooper E.E. and Hatfield J.L.: 2001: Correlation of Human Olfactory Responses to Airborne Concentrations of Malodorous Volatile Organic Compounds Emitted from Swine Effluent. Journal of Environmental Quality. Vol 30, Mar-April (2001).