Further Investigation of the Performance of the XSD MINICAMS®

Update on a Topic Presented at CWD2014

Pueblo Chemical Agent-Destruction Pilot Plant

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CWD 2015 ***June 5, 2015***

Acronyms

ABCDF	Aberdeen Chemical Agent Disposal Facility
ACWA	Assembled Chemical Weapons Alternatives
BGCAPP	Blue Grass Chemical-Agent Disposal Facility
DELCD	Dry electrolytic conductivity detector
FAL	Found action level
GC	Gas chromatographic; gas chromatography
H	Chromatographic peak height
H_{CAL}	Chromatographic calibration peak height
HD	Agent mustard
LMQAP	Laboratory and Monitoring Quality Assurance Plan
LOQ	Limit of quantification
n	Exponent used within the MINICAMS; n = 1.00 for a linear detector
nA	Nanoamperes
OICO	O.I. Corporation
P&A	Precision and accuracy
PCAPP	Pueblo Chemical Agent-Destruction Pilot Plant
PM	Preventive maintenance
TAL	Target action level
UIFM	Uncertainty in found mass
VSL	Vapor screening level
XSD	Halogen Specific Detector

MINICAMS® with a Halogen Selective Detector (XSD)

PCAPP

- Sensitive with a typical detection limit of < 0.5 ng for agent mustard (HD)
- Selective by a factor of about 8,000 for chlorinated compounds vs. hydrocarbons
- Used for monitoring HD, Lewisite, and other chlorinated agents since about 1996
- Used during the destruction of agent mustard at the Aberdeen Chemical Agent Disposal Facility (ABCDF), 2003-2006
- Will be used during the destruction of agent mustard at the Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) and at the Blue Grass Chemical Agent-Destruction Pilot Plant (BGCAPP)
- Previously assumed to be a linear detector in demilitarization applications

XSD MINICAMS

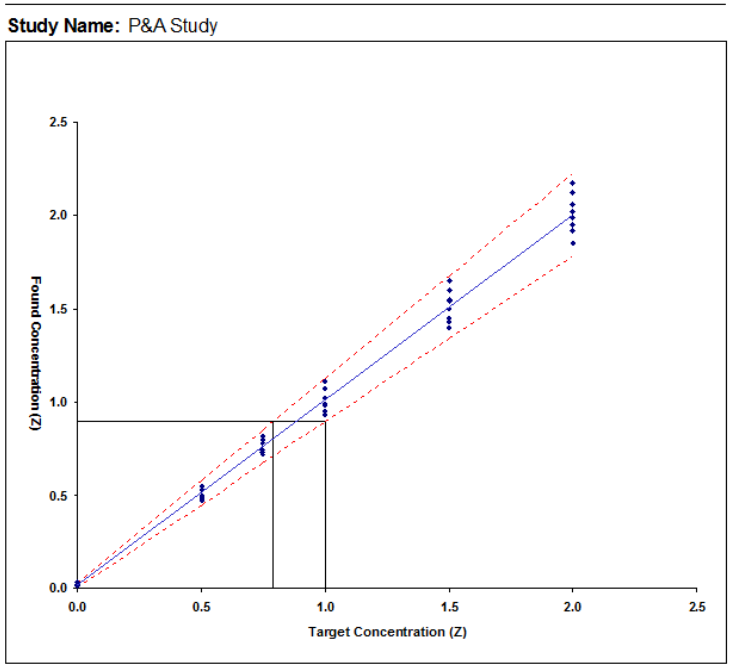
ABCDF

PCAPP
Pueblo Chemical Agent-Destruction Pilot Plant

MINICAMS® is a registered trademark of CMS Research Corporation, Pelham, Alabama.

Requirements for Certification and Validation of an Air Monitoring System and Method*

- **Certification** at U.S. agent destruction sites requires
  - —passing a precision-and-accuracy (P&A) study consisting of a series of challenges conducted twice per day over a 4-day period
  - —passing an initial baseline study consisting of at least one challenge per day over a 28-day period
- **Validation** requires
  - —passing a continuing baseline study consisting of at least one challenge per day evaluated each 28-day period



*ACWA Programmatic Laboratory and Monitoring Quality Assurance Plan

Pueblo Chemical Agent-Destruction Pilot Plant

Requirements at the Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP)

- **Certification by**

  —passing a precision-and-accuracy (P&A) study in the range of 0.2 to 2 VSL for HD (vs. the normal range of 0.5 to 2 VSL)

  —passing statistical requirements for an initial baseline study consisting of at least one challenge per day over a 28-day period

- **Demonstrating a limit of quantification (LOQ) of < 0.2 VSL**
  (Note that some decisions at the site will be made on the basis of MINICAMS concentration reports that are >0.2 VSL—versus greater than a true concentration of 0.2 VSL.)

- **Validation by**

  —passing a continuing baseline study consisting of at least one challenge per day evaluated statistically each 28-day period

1.0 VSL = 0.003 mg/m^3

Equivalent to 4.05 ng at PCAPP (for a sample flow rate of 450 mL/min and a sample period of 3 min)

Equations Relating Peak Height to Concentration in the MINICAMS Code

The equation used in the MINICAMS software to relate peak height (H) to concentration for calibration at a single challenge concentration (1.00 VSL) is:

$$H = H_{CAL} \ (VSL)^{n}$$

where

H_{CAL} is the average peak height obtained for 1.0-VSL challenges (i.e., for a single-point calibration)

and

n is a coefficient, which is set to 1.00 for an assumed linear response.

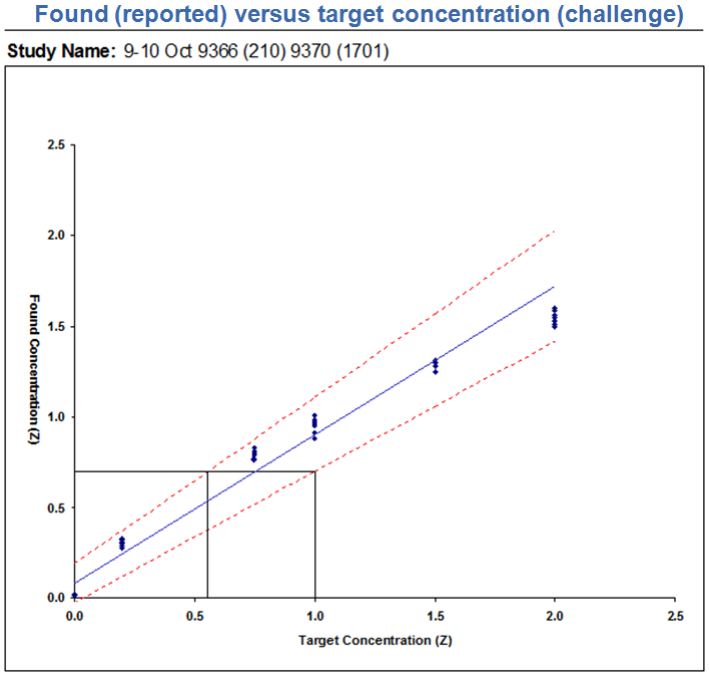
For a given peak height, the concentration reported by the MINICAMS is given by:

$$VSL = (H/H_{CAL})^{1/n}$$

CERTIFY Results for PCAPP P&A Study
Oct 9-10, 2013, assuming linearity (i.e., n = 1.00)

Preliminary study conducted over two days to get an indication of MINICAMS performance

- **Calibrated two XSD MINICAMS units using two 1.0-VSL-equivalent injections for each**
- **A series of 6 challenges of each MINICAMS was conducted twice per day over a 2-day period (0.0, 0.2, 0.75, 1.0, 1.5 and 2.0 VSL)** —48 challenges
- **P&A study passed requirements in the PCAPP LQCP, but UIFM (23%) marginal** —raising PCAPP concerns about the robustness of the method
- **PCAPP goal of LOQ < 0.2 VSL was not met**
- **Accuracy less than optimum** —found concentrations high at less than 1.0 VSL and low at greater than 1.0 VSL



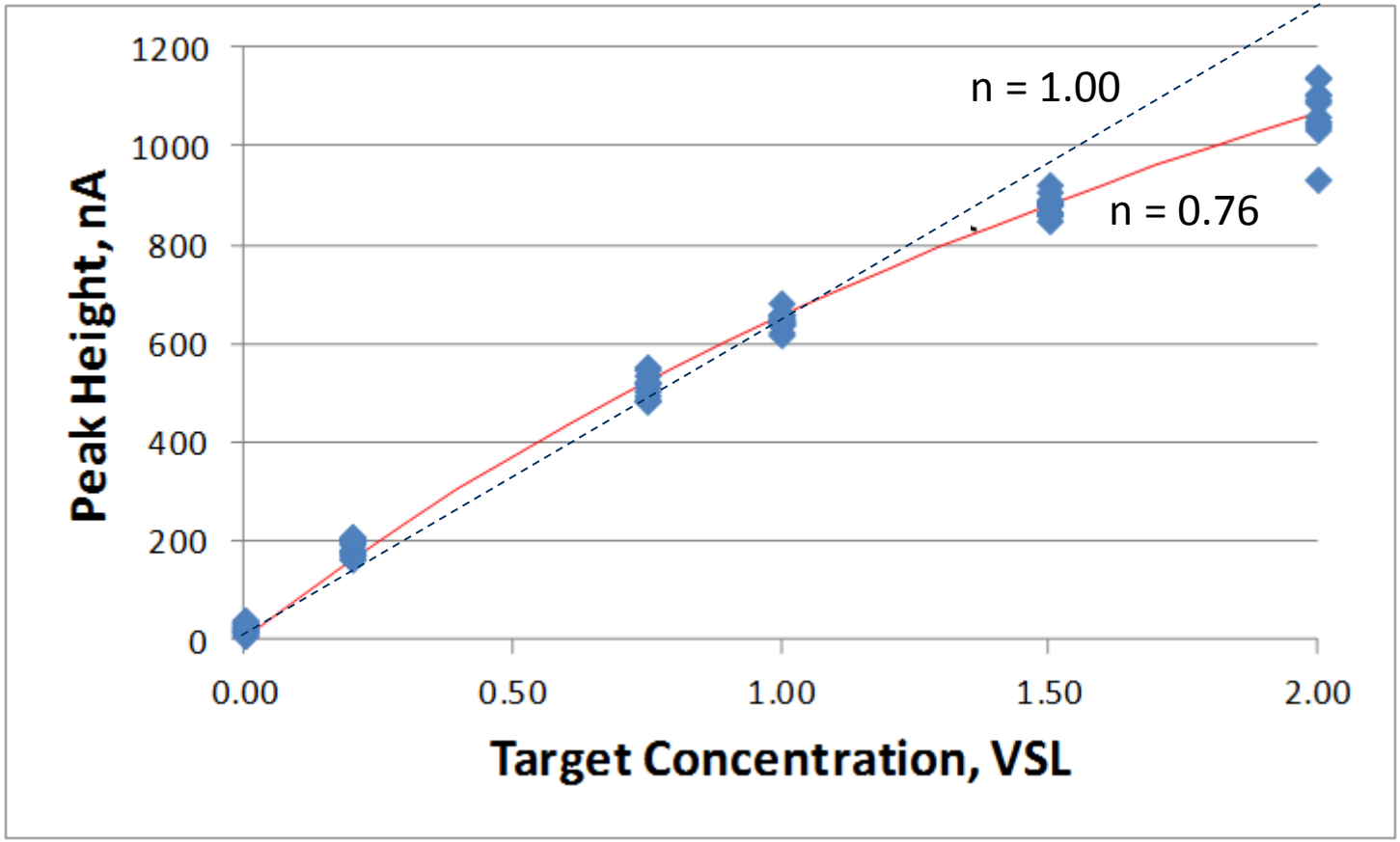
FAL:	0.6972
TAL:	0.5539
LOQ:	0.3018
DETL:	0.1344
DECL:	0.1929
UIFM:	22.67 %
UIAS:	22.28 %

Slope:	0.8186
Y-intercept:	0.0829
Percent Recovery:	90.15 %
Data Points:	48

n = 1.00

Pueblo Chemical Agent-Destruction Pilot Plant

Analysis of Initial Response Curves Obtained at PCAPP Yielded an Exponent Value of n = 0.76



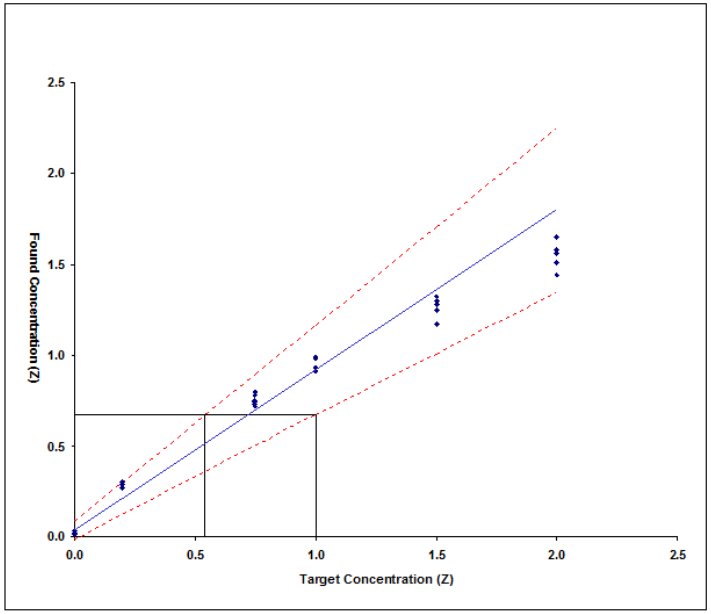
CERTIFY Results for a PCAPP P&A Study

Nov 20-23, 2013, assuming linearity (i.e., n = 1.00)

PCAPP

Conducted in accordance with all requirements in the ACWA LMQAP

- Calibrated two XSD MINICAMS units using two 1.0-VSL injections for each
- A series of 6 challenges of each MINICAMS was conducted twice per day over a 2-day period (0.0, 0.2, 0.75, 1.0, 1.5 and 2.0 VSL) —48 challenges (plus 0.5-VSL challenges)
- 6 different standard solutions; 2 µL injected for each challenge; blind, randomized challenges
- P&A study failed UIFM (27%)—raising PCAPP concerns about the robustness of the method
- PCAPP goal of LOQ < 0.2 VSL was met
- Accuracy less than optimum—found concentrations high at less than 1.0 VSL and low at greater than 1.0 VSL



FAL:	0.6711	Slope:	0.8796
TAL:	0.5412	Y-intercept:	0.0395
LOQ:	0.1426	Percent Recovery:	91.91 %
DETL:	0.0559	Data Points:	48
DECL:	0.0887		
UIFM:	26.98 %		
UIAS:	22.93 %		

n = 1.00

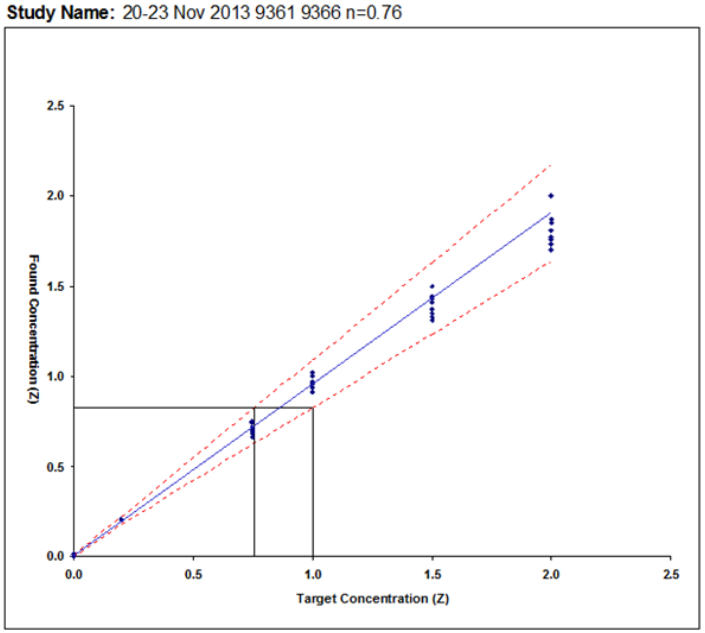
Pueblo Chemical Agent-Destruction Pilot Plant

CERTIFY Results for PCAPP P&A Study

Nov 20-23, 2013, assuming non-linearity (n = 0.76)

Conducted in accordance with all requirements in the ACWA LMQAP

- Calibrated two XSD MINICAMS units using two 1.0-VSL injections for each
- A series of 6 challenges of each MINICAMS was conducted twice per day over a 2-day period (0.0, 0.2, 0.75, 1.0, 1.5 and 2.0 VSL) —48 challenges
- 6 different standard solutions; 2 µL injected for each challenge; blind, randomized challenges
- P&A study passed, UIFM of 14%
- PCAPP goal of LOQ < 0.2 VSL was met
- Accuracy improved significantly



FAL:	0.8254
TAL:	0.7590
LOQ:	0.0137
DETL:	0.0070
DECL:	0.0136
UIFM:	13.69 %
UIAS:	12.05 %

Slope:	0.9493
Y-intercept:	0.0070
Percent Recovery:	95.63 %
Data Points:	48

n = 0.76

Pueblo Chemical Agent-Destruction Pilot Plant

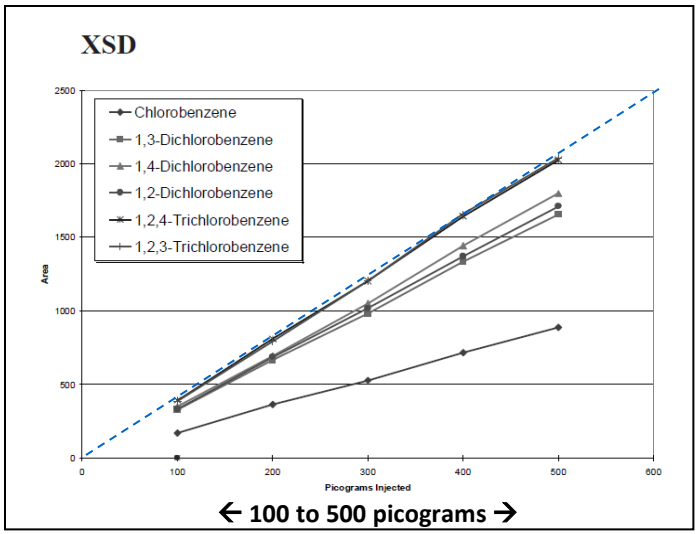
Investigation of Non-Linearity of the XSD

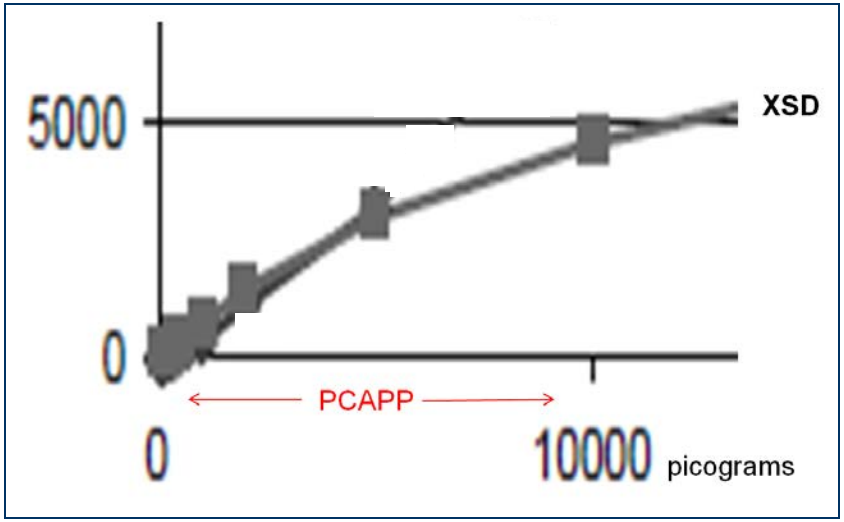
- OICO Applications Note
- OICO Technical Note
- Another detector based on the same technology as the XSD
- Statistical analysis of data for 125 challenge series of 17 different MINICAMS units at PCAPP
- Challenge data for HD and simulant chemicals at PCAPP and other sites
- Nine-month study for 3 MINICAMS units operating 24/7 at PCAPP

OICO Applications Note for the XSD

- **Response linear and through origin (0,0) only at low masses**
- **Response non-linear at higher masses**

XSD Reactor Probe Assembly





OICO Applications Note 16561101, entitled *"Using the Halogen Specific Detector (XSD™) as an Alternative to the ELCD in USEPA Methods"*

OICO Notes on Operation of the XSD

September 2, 1994 – Dr. Rich Simon, Developer of the XSD at OICO

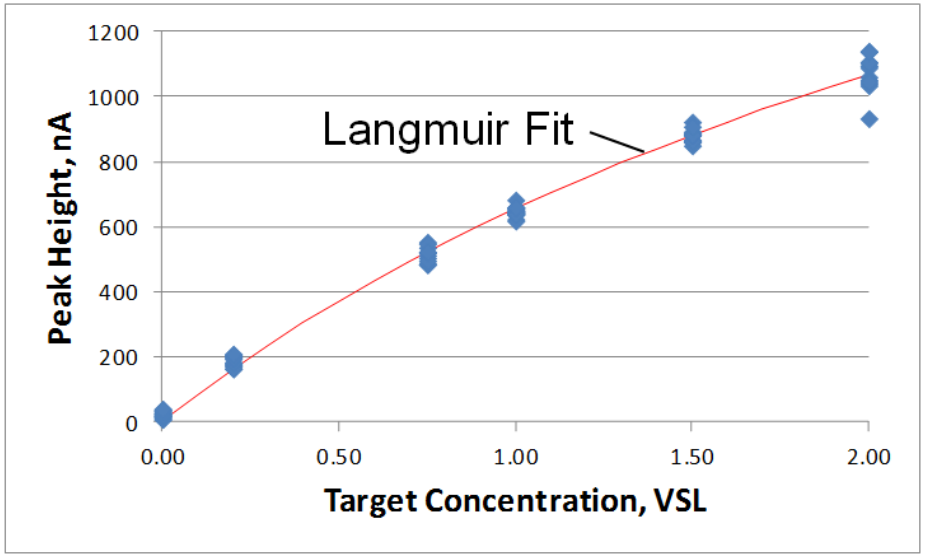
The detector response correlates with simple Langmuir adsorption (i.e. fixed number of adsorption sites, at equilibrium a fraction of the sites (Z) is occupied by adsorbed species, each site can adsorb only 1 atom, heat of adsorption is the 'same' for all sites (and independent of the fraction covered), and no interaction between species at different or neighboring sites). Let B equal the ratio of the adsorption rate to the desorption rate (i.e. commonly call the adsorption coefficient), then $Z = bP/(1+bP)$. At low partial pressures of atomic chlorine, $bP \ll 1$ so $Z = bP$ (i.e. adsorption is a linear function of the partial pressure of atomic chlorine). At higher pressures, $1 - Z = 1/(bP)$ -- the fraction of available sites becomes inversely proportional to the partial pressure of atomic chlorine.

Langmuir adsorption model

$$H = \frac{\alpha\ (VSL)}{1 + \beta\ (VSL)}$$

where α and β are constants

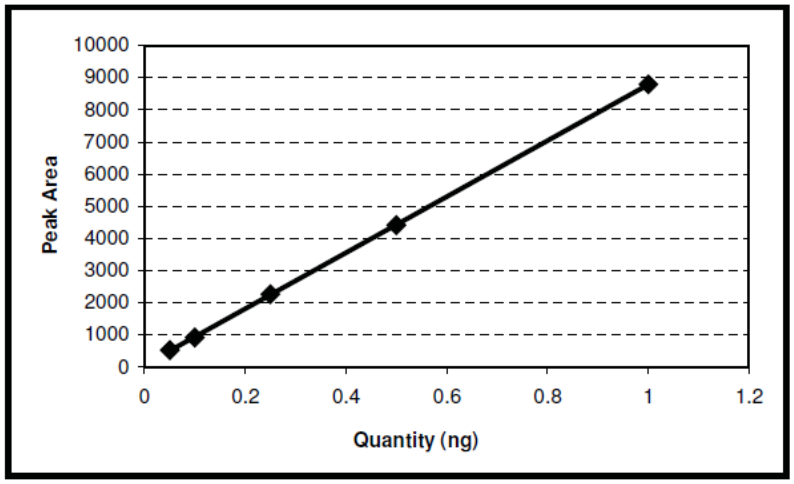
At PCAPP 4.05 ng Corresponds to 1.00 VSL*



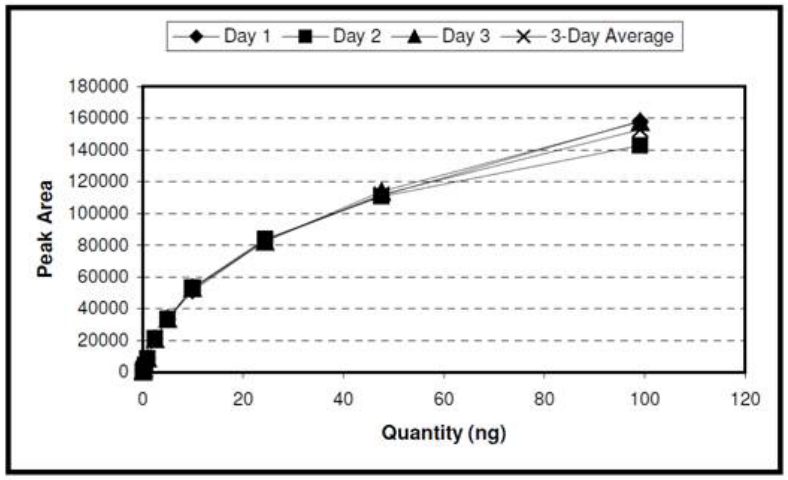
*For a sample flow rate of 450 mL/min and sample period of 3 min

Another Detector (Not Used at PCAPP But) Based on the Same Technology as the XSD

- **Manufactured by SRI Instruments (Las Vegas, Nevada)**
- **Sold as the Dry Electrolytic Conductivity Detector (DELCD)**
- **Response linear and through origin (0,0) only at low masses**
- **Response non-linear at higher masses**

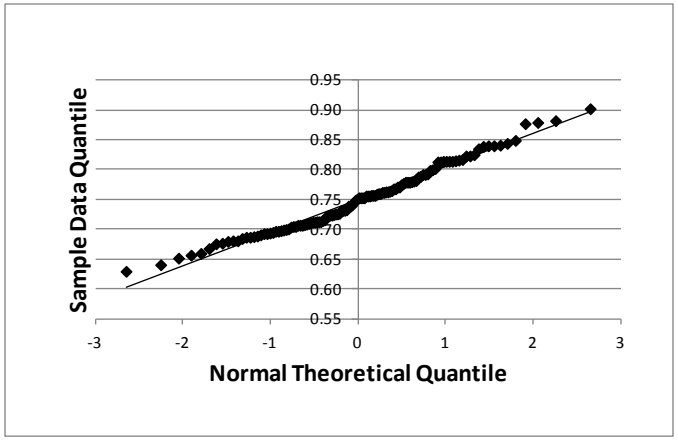


Data from Xiaojing Li (2009)



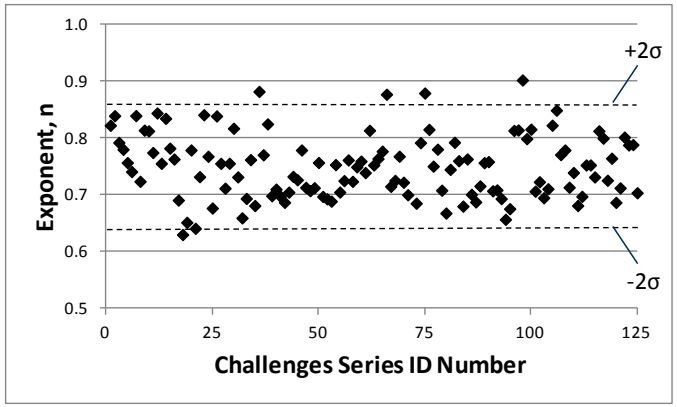
Data from Xiaojing Li (2009)

125 Data Sets Generated at PCAPP Were Analyzed Statistically



QQ Plot

Test of exponent values data set for normality



Distribution of exponent values determined

Statistical results:

Parameter	125 Data Sets[1]
Average exponent (n)	0.75
Avg correlation coefficient	0.996
Standard deviation	0.056
95% Confidence interval	0.64 to 0.86
Minimum exponent value	0.63
Maximum exponent value	0.90

[1]Challenge series (125 each) for 17 different MINICAMS units, conducted Oct 9, 2013, through Jan 16, 2014.

Data Sets Reviewed from Various Sites

For HD and Other Chlorinated Chemicals and Another Detector Based on the Same Technology as the XSD

Test Site	Challenge Chemical	Equivalent HD Range, VSL[1]	Average Exponent	Instrument Type Tested	Number of Instruments	Number of Series[2]
OICO (Texas)	Chloroform	0.99 to 4.94	**0.68**	GC with XSD	1	1
OICO (Texas)	Chlorobenzene	0.35 to 1.74	**0.71**	GC with XSD	1	1
OICO (Alabama)	Dichlorvos	0.09 to 0.67	**0.92**	XSD MINICAMS	8[3]	32
PCAPP	Dichlorvos	0.25 to 2.0	**0.77**	XSD MINICAMS	1	1
NRT Methodologies	Dichlorvos	0.5 to 2.1	**0.83**	XSD MINICAMS	2	2
PCAPP	HD	0.2 to 2.0	**0.75 ± 0.11**	XSD MINICAMS	17	125
BGCAPP	HD	0.5 to 2.0	**0.78**	XSD MINICAMS	4	16
ECBC	HD	0.5 to 2.0	**0.88**	XSD MINICAMS	4	16
ABCDF	HD	0.2 to 3.0	**0.85**	XSD MINICAMS	2	9
Univ of Waterloo[4]	Aroclor 1254 (PCBs)	0.3 to 3.0	**0.77**	GC with DELCD	1	3
BEST Center	1-Chlorodecane	0.33 to 2.67	**0.76**	AMS with DELCD[5]	10	52

[1]HD-equivalent challenge range, based on chlorine content, a sample flow rate of 450 mL/min, and a sample period of 3 min.

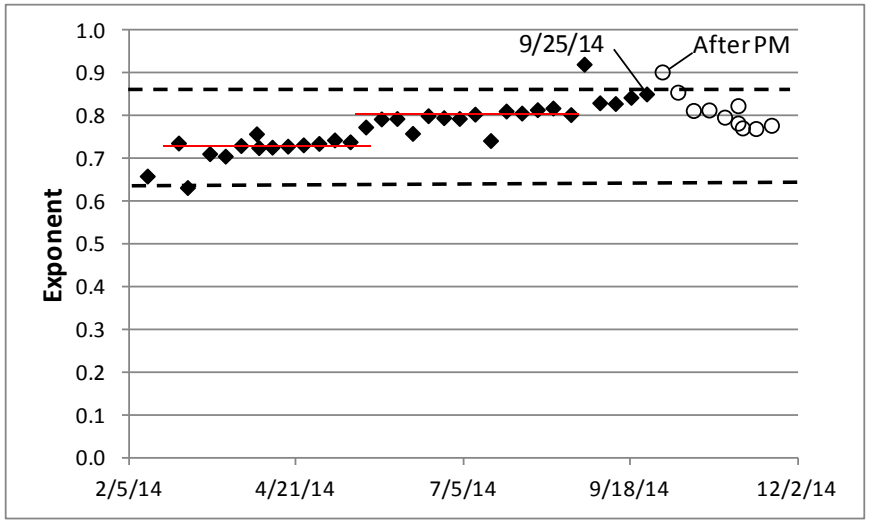
[2]Number of challenge data series analyzed for each site.

[3]All PCAPP XSD MINICAMS units underwent P&A studies at OICO; only eight representative challenge data sets were reviewed.

[4]From Thesis for Master of Science in Chemistry, University of Waterloo, Xiaojing Li, 2009 (*Ref.5)*.

[6]Automated air monitoring system (AMS) developed by Battelle (Aberdeen, Maryland) with a DELCD (same technology as the XSD).

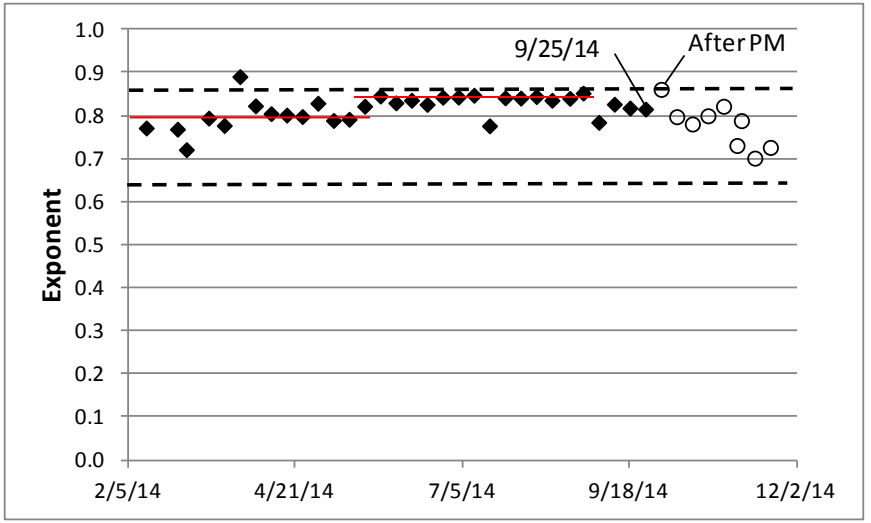
Exponent Values Obtained During a 9-Month Study at PCAPP*



Serial No. 9358

PM included replacing the XSD reactor probe assembly

Serial No. 9616



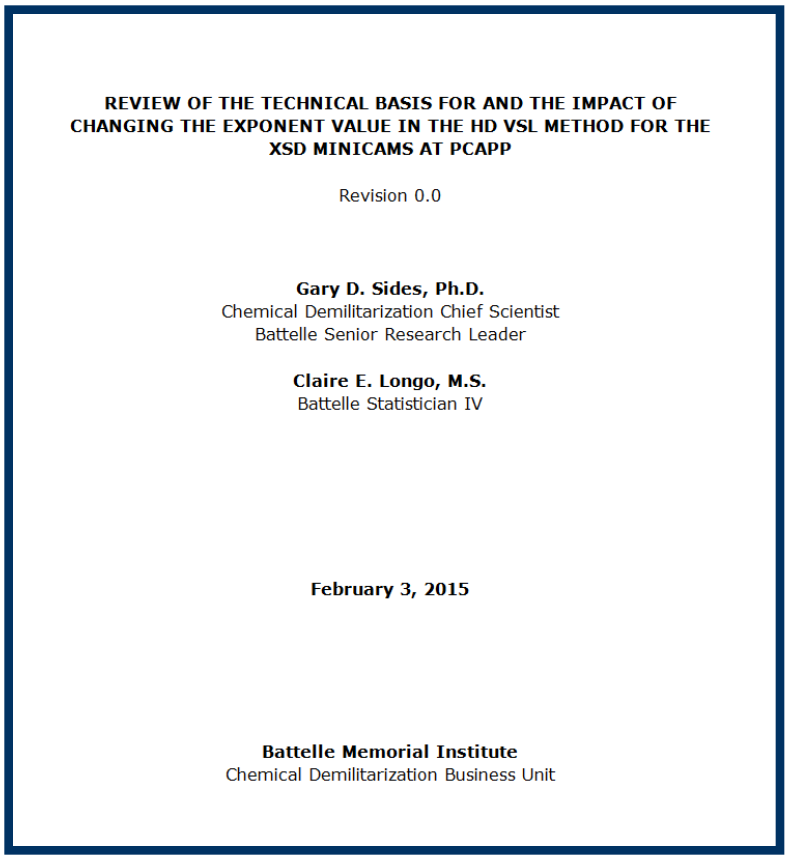
*Three XSD MINICAMS units were operating 24/7 and challenged weekly in the range of 0.2 to 2.0 VSL.

Statistical Results for the 9-Month Study
Compared to the 125 Data Sets Analyzed Previously

Parameter	125 Data Sets[1]	S/N 9358[2,3]	S/N 9616[2,3]	S/N 9000[2,3]
Average exponent (n)	0.75	0.78	0.81	0.80
Avg correlation coefficient	0.996	0.999	0.999	0.999
Standard deviation	0.056	0.057	0.040	0.068
95% Confidence interval	0.64 to 0.86	067 to 0.89	0.73 to 0.89	0.66 to 0.94
Minimum exponent value	0.63	0.63	0.70	0.65
Maximum exponent value	0.90	0.92	0.89	0.90

[1]Challenge series (125 each) for 17 different MINICAMS units, conducted Oct 9, 2013, through Jan 16, 2014.
[2]Challenges series for 3 different MINICAMS units conducted weekly from Feb 13 through Nov 20, 2014.
[3]Each of the MINICAMS units passed a P&A study after the end of the 9-month study.

Work Regarding the Response of the XSD MINICAMS Summarized in a Recent Report



REVIEW OF THE TECHNICAL BASIS FOR AND THE IMPACT OF CHANGING THE EXPONENT VALUE IN THE HD VSL METHOD FOR THE XSD MINICAMS AT PCAPP

Revision 0.0

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February 3, 2015

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Summary

PCAPP

- The response of the XSD was previously assumed to be linear in demilitarization applications—in fact, the response of this detector correlates with Langmuir adsorption, which is non-linear.
- Literature from the manufacturer of the XSD (OICO) indicates that the detector is non-linear in the mass range of interest at PCAPP.
- Reviews of challenge data for eleven different combinations of sites and chemicals and two different detectors based on the same technology (XSD and DELCD), as well as additional literature reviews, confirmed the non-linearity of the XSD.
- The non-linear response of the XSD can be modeled over the concentration range of interest for the VSL method at PCAPP (0.2 to 2.0 VSL) using the equation $H = H_{CAL} (VSL)^{n}$ with the exponent value, n, set to 0.76.
- P&A studies conducted with the exponent, n, set to 0.76 yielded greatly improved results and limits of quantification less than the PCAPP target of < 0.2 VSL.
- Although some variation of the exponent values obtained were noted during a 9-month study using three MINICAMS units, these MINICAMS units passed P&A studies at the end of the test period with the exponent value at 0.76.