Development and Evaluation of a Portable Gas Chromatograph-Mass Spectrometer Based Field Test Method

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ABSTRACT

This paper details the process of developing and evaluating a portable gas chromatograph-mass spectrometer based field test method using an iterative five-step approach. The approach termed the General Approval Process was developed as a means to assist instrument developers and others interested in demonstrating the applicability of new test methods and instrumentation. This approach has been accepted by The EPA as an alternate to conducting innumerable Method 301 validation tests, particularly for those methods that are capable of simultaneous multicomponent analysis from numerous source matrices.

INTRODUCTION

Leybold Inficon (Inficon) developed the HAPSITE™, a portable gas chromatograph-mass spectrometer (GCMS) for conducting gas phase measurements of volatile hazardous air pollutants. They contracted Emission Monitoring Inc. (EMI) to assist in the development effort and to conduct independent laboratory and field testing of the instrumentation. A test method for stationary source applications was written after extensive laboratory evaluation, and has been utilized at numerous manufacturing facilities producing valuable on-site measurement results. The GCMS test method provides measurements of volatile organic compounds at concentration levels approximating 20 parts per billion in a direct extractive mode of operation. Applications are easily extended to conduct ambient measurements. As part of the GCMS field test method, results must be available on-site after each GCMS sample run so that those interested have the opportunity to make decisions regarding additional testing, process control decisions, or whether an area is unsafe for occupational exposure.

During the initial stages of the instrument development process, the Office of Air Quality Planning and Standards-Emission Measurement Center of the U.S. EPA was requested to provide input regarding the conditions under which a source test method specific for direct interface extractive GCMS could be applied at different stationary source categories. The EPA implied that Method 301 was the only way to validate new test methods. Because a GCMS is capable of measuring multiple compounds simultaneously from a virtually unlimited number of sources, and because an indefinite number of Method 301 validation tests are cost prohibitive, and do not demonstrate adequately the capabilities of a direct interface multicomponent test method, EMI and Inficon developed the General Approval Process for new test methods. The EPA agreed to the General

Approval Process as an alternate means to validate new test methods, provided that other interested parties and instrument developers could use the process as well.

The General Approval Process[1] is an alternative to EPA Method 301 and other method validation processes, and employs five steps that evaluate fully a new test method. These steps are iterative and consist of; 1) full disclosure of a particular test method's strengths and weaknesses, 2) a basic laboratory evaluation, 3) an extended laboratory evaluation, 4) field testing (including limited Method 301 validation testing), and 5) submission of the entire process results to the EPA or regulating authority, and petition for approval. This process is designed to use valid scientific and engineering principals to evaluate a candidate measurement technique, and to use the information gained during the course of the process to formulate a test method that has adequate quality assurance and quality control to gather meaningful measurement results.

This paper discusses a specific case example of the General Approval Process as applied to the direct interface GCMS field test method[2] , and the HAPSITE GCMS. Important findings and field test measurement results specific to the analyzer are provided along with recommendations for application of the General Approval Process to other new test method developers.

BACKGROUND

Discussions with EPA representatives regarding this project commenced in March 1994. Initially, it was hoped that minor modifications to the repeatability requirements of Method 18 (40CFR60, Appendix A) could be made to accommodate the direct interface GCMS method which offered great advantages including; 1) the ability to positively identify and quantify numerous volatile organic compounds, 2) much lower detection limits than other direct interface test methods, and 3) the use of commercially prepared calibration standards. Discussions with EPA indicated that it was extremely unlikely that they would accept any modifications to Method 18. Even though source-by-source approval of any method is far too expensive and time consuming, the EMC representatives explained that no other means of evaluating new test methods was available other than repeated Method 301 validation tests.

Based on additional discussions with EPA, EMI and Inficon developed an alternate approach. Two documents were submitted to EMC in August of 1995; the General Field Test Method Approval Process, and Specific Case Example: Field Test Method Approval Process for Direct Interface GCMS Method. These documents included; 1) a five-step iterative process for the demonstration of new test methods (that would be made available to any instrument developer that wanted to utilize this process), 2) pertinent information regarding the GCMS technology, potential problem areas and concerns, 3) detailed descriptions of the GCMS analyzer and sample interface, and a generic direct interface GCMS test method formatted according to EPA requirements, 4) a basic laboratory evaluation plan, and 5) a preliminary plan for extended laboratory and field evaluations. EPA reviewers provided comments on the initial submission during subsequent meetings and one reviewer provided written comments. EPA's participation in the project was outlined in a letter from The EPA, OAQPS, EMC in December 1995.

Numerous laboratory tests and two field ruggedness tests were performed from October 1995 through October 1996. Also during this period, substantial changes to the GCMS software were made that affected the operation and performance of the measurement system. Additional changes and modifications to the hardware were also made as the instrument evolved and various problems were identified and resolved. Much practical experience and insight was gained in the

performance of preliminary tests, and in the attempt to conduct the iterative process. Studies were performed by the supplier of gaseous internal standards to improve the manufacturing process and to determine the accuracy and stability of the standard values. Also, the prototype sample interface designed and constructed by EMI was replaced with a commercially available system built by Clean Air Engineering.

A revised and updated Initial Disclosure and Method Proposal were provided to EPA in October 1996. The revised disclosure statement was updated to reflect changes in the measurement system and its operation and to respond to comments from EPA reviewers. A revised GCMS direct interface method and revised laboratory and field evaluation test plans were also included in this submission to EPA.

Laboratory evaluations of the GCMS production model and the commercially available sample interface were performed during October, November, and December of 1996. A field test plan for a formal Method 301 evaluation was also submitted to EPA in October 1996. The EPA was contacted prior to the test, to extend comments on the test plan and to observe the field test activities. The field tests were conducted November 12-15, 1996 on the trona calcining emission stacks and on the mine exhaust vent at the Solvay Minerals Inc. facility located near Green River, Wyoming.

A report presenting the results of the Method 301 demonstration tests conducted at Solvay was submitted to the EPA EMC in February 1997 along with a letter requesting that EPA formally determine the sources and compounds for which the method was valid. Also included in the February letter was a request to include the direct interface GCMS method on EPA's published list of validated methods.

A report describing the results of the activities in this three-year evaluation process was submitted to the EPA Emission Measurement Center in July 1997 as the fifth and final step in the General Approval Process. Specifically, EPA was requested to accept the direct interface GCMS test method as a valid, alternate test method for measuring volatile organic hazardous air pollutants. After some deliberation and negotiation, acceptance of the GCMS test method by the EPA was announced in October 1997. The method and supporting documentation are available on the EPA Website.

THE GENERAL APPROVAL PROCESS - Specific Case Example

The plan for conducting a comprehensive evaluation of the GCMS test method and HAPSITE instrumentation entitled Specific Case Example: Field Test Method Approval Process for Direct Interface GCMS Method included a complete description of the analyzer, the sample interface system, and a full disclosure about its operation and potential application for conducting emission tests. Submission of this document to the EPA satisfied item 1 of the general approval process.

Basic laboratory evaluations were performed to determine; 1) the accuracy and stability of calibration materials, 2) the stability of the mass spectrometer with time and the fundamental MS tuning criteria, 3) the instrument analytical function (i.e., precision, concentration measurement range, and accuracy for 36 the target analytes listed in the field test meted), 4) sampling system performance (i.e., response time, carryover, and integrity), and 5) the overall operational reliability of the measurement system. These evaluations represented step two in the five step iterative process.

Extended laboratory investigations were conducted to determine the effect of varying moisture concentrations on the performance of both the analyzer and the sampling system, and potential analytical interferences (cross-interference) among the 36 target compounds. These evaluations represented step three in the five step iterative process.

Several field ruggedness tests were conducted of the measurement system. These tests demonstrated the reliability of the system, its overall ruggedness and ability to withstand the rigors of shipping, and its suitability for field use. In addition, Method 301 demonstration tests were performed at a mineral calcining facility and at a mine vent. Effluent matrices at these test sites represented some of the most difficult measurement conditions that could be encountered in the application of a GCMS-based measurement system. These evaluations represented step four in the five step iterative process.

An extensive engineering report describing the results of all steps in the General Approval Process was prepared. The engineering report presented the results of all testing, including those tests that challenged to analyzer to the point of failure. This step is of fundamental importance in this process because it demonstrates the test method's validity over the range of applications. The developer or interested party must disclose fully the expected performance and limitations of the instrument or method, and the report must present the results from testing that challenges the performance specifications. The General Approval Process allows sound scientific and engineering judgment to replace simple empirical tests that are conducted repeatedly and that often do not evaluate a particular methods strength and/or weakness.

IMPORTANT FINDINGS OF APPROVAL PROCESS - Specific Case Example

Because of the iterative nature of the process, many of the basic laboratory experiments were repeated after instrumental design modifications. Testing of alpha production units pointed to areas where improvements could be made in the instrument design. Many of the instrument modifications were enacted to improve the sensitivity for the 36 target analytes, and to increase ease of operation.

The extended laboratory evaluation tested beta production units and challenged the instrument under simulated field testing and actual field testing environments. Results from the extended laboratory evaluation indicated that the GCMS was exceptionally stable with respect to retaining calibration for the 36 target analytes with time, and could withstand shipping and field conditions.

The Method 301 validation testing proved the repeatability and accuracy of the instrumentation under difficult conditions that represent some of the greatest challenges for a GCMS; high moisture effluent, numerous analytes and co-eluting peaks, and high and variable concentrations of volatile and semi-volatile hydrocarbons.

The submission of the engineering report to the EMC and the petition for alternate test method approval proved to be the most difficult step of the process. It was initially hoped that involving the EPA in each step of the process, and providing all the results from all testing would enable a decision regarding the GCMS test method applicability. Because of the precedent setting nature of this project, The EPA was reluctant to give wide ranging approval of the GCMS Method to sources other than that where the Method 301 testing was conducted successfully. This was exactly what EMI and Inficon had hoped to avoid, and the reason for developing the General

Approval Process. Many ensuing discussions were held with EPA-EMC representatives regarding alternate test method approval on a wider basis other than the Method 301 test. After lengthy negotiation, and some lively discussions between interested parties, The EPA granted alternate test method approval to the GCMS field test method in October 1997.

The following items represent the overall conclusions that are specific to the HAPSITEÖ analyzer in the course of following the General Approval Process.

1. The evaluation demonstrated that a direct interface GCMS test method has been developed in the private sector and can be implemented through the use of commercially available instrumentation to produce accurate, precise, and reliable emission measurements of a wide range of volatile organic compounds.

2. The specific GCMS measurement system evaluated during this project meets and exceeds the performance criteria of Method 18 and may therefore be used in many regulatory applications. In addition, the direct interface GCMS test method provides for collection of higher quality data than does Method 18.

3. Solvay Minerals used the GCMS data from the Method 301 validation study as part of their permit application process and to demonstrate to the State of Wyoming the absence of chlorinated hydrocarbons in their calciner effluent.

4. The direct interface GCMS test method and measurement system allows for the positive identification of both target analytes and unknown compounds in stationary source effluent streams and eliminates costly trial and error approaches and cumbersome pretest sampling and analysis.

5. The direct interface GCMS test method and measurement system extends the range of accurate and reliable on-site measurements for volatile organic compounds to concentrations much below 100 ppb; much lower levels than attainable by any other direct interface method.

6. The direct interface GCMS test method and performance criteria have been validated through extensive laboratory testing, Method 301 validation tests, and alternative validation approaches. The direct interface measurement system operated in accordance with the method provides effluent measurement results with a precision of 5% and bias of 10% at concentrations approximating 1 ppm.

7. The direct interface GCMS test method provides near real-time measurement results allowing for effective on-site decision making and tracking of effluent concentration variations.

8. The direct interface measurement system, operated in accordance with the method, was demonstrated to meet or exceed the performance requirements and data quality objectives of the method, and retained its calibration for 36 target analytes over a two month period after repeated shipping.

9. Six calibration check surrogates were proven to be adequate to verify the calibration status of the GCMS measurement system for the 36 target analytes. This greatly reduces the amount of calibration standards necessary for shipping to the field.

Tables 1 and 2 present the method target analytes and calibration check surrogates. Table 3 and Figures 1-8 demonstrate the calibration stability of the direct interface GCMS measurement system, and the efficacy of the calibration check surrogate compounds.

RECOMMENDATIONS

The General Approval Process is beneficial when attempting to gain regulatory approval of a new test method, or measurement technique that has multicomponent capabilities and broad ranging applicability, and where other verification processes are too costly. The primary reasons for developing a new method are: 1) to replace existing methods that are used to demonstrate compliance with existing emissions standards (where the new method is less expensive or quicker), 2) to satisfy new measurement requirements brought about by new regulatory actions and standards, 3) to enable measurements that verify or regulate certain process operations, 4) to provide a needed measurement that has never before been available, or 5) to accompany a new measurement technique or new instrumentation. In many cases, the cost of developing new test methods and instrumentation supersede the requirements to conduct the actual measurements. Therefore, a carefully examination of the methods end use is recommended before endeavoring the General Approval Process or any other method validation approach.

It is important to obtain the interest and participation of those parties that will eventually be requested to approve the method and decide its applicability. Many times the barrier to acceptance of new methods and instrumentation is the regulating agency that does not understand the methods applicability, its ability to fulfill some measurement requirement, or technical knowledge that may be derived from its use. Certainly the developers are the most knowledgeable about a test methods particular strengths and weaknesses. It is their responsibility to educate and to communicate to those who are in the position to decide the applicability of the method, or who are in the position to promulgate new emission test methods. It is only then that consensus organizations, instrument developers, and other private sector groups may effectively break down the barriers for new test method acceptance, and thus use of new instrumentation.

REFERENCES

1. Peeler, J.W., Kinner L.L., and DeLuca, S., 1996. General Field Test Method Approval Process and Specific Application for a Direct Interface GCMS Source Test Method, *Proceedings Air & Waste Management Association*, Nashville, TN, paper no. 96-RP132.01.

2. Peeler J.W., Kinner L.L., Development of a Direct Interface GCMS Source Test Method, *Proceedings Air and Waste Management Association Clean Air '96 Specialty Conference*, Orlando, FL.

Table 1. Target Analytes and CAS Numbers Specific to GCMS Test Method

Benzene-71432	cis-1,2-Dichloroethene-156592	Carbon Tetrachloride-56235
Bromodichloromethane-75274	Dibromochloromethane-124481	Chlorobenzene-108907
Carbon DisulfIde-75150	1,1-Dichloroethane-75343	cis-1,3-Dichloropropene-10061015
Chloroform-67663	1,2-Dichloropropane-78875	1,2,-Dichloroethane-156592
Methyl iso-Butyl Ketone-108101	Ethyl benzene-100414	1,1-Dichloroethene-75354
Styrene-100425	Ethyl chloride-75003	trans-1,2-Dichloroethene-156605
Tetrachloroethylene-127184	Methylene Chloride-75092	Methyl Ethyl Ketone-78933
Toluene-108883	1,1,2,2-Tetrachloroethane-79345	2-Hexanone-591786
Bromoform-75252	1,1,1-Trichloroethane-71556	trans-1,3-Dichloropropene-542756
Vinyl Acetate-105084	1,1,2-Trichloroethane-79005	Trichloroethene-79016
Vinyl Chloride-75014	p-Xylene-106423	m-Xylene-108383
Chloromethane-74873	Bromomethane-74839	o-Xylene-95476

Table 2. Calibration Check Surrogates

COMPOUND	CLASS REPRESENTING	MOLECULAR WEIGHT	QUANT-ION	RETENTION TIME
Methylene Chloride	Chlorinated	84	84	2:41 mins
Methyl Ethyl Ketone (MEK)	Polar	72	72	2:57 mins
Carbon Tetrachloride	Chlorinated	152	117	3:35 mins
Toluene	Aromatic	92	91	5:08 mins
Chlorobenzene	Chlorinated Aromatic	112	112	7:22 mins
O-Xylene	Aromatic	91	91	9:44 min