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Performance of a gas chromatograph–atomic emission detector system in a mobile analytical laboratory[☆]

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Abstract

The effect of ambient environmental conditions on a gas chromatography–atomic emission detection (GC–AED) system was characterized. The environmental stimuli was shock and vibration due to operating the hardware in a mobile analytical laboratory. The effect of large temperature change was also examined. System performance using a reference sample and operational recommendations are given.

Keywords: GC–AED; AES; Mobile analytical laboratory; On-site analysis

1. Introduction

The ability to perform on-site chemical analysis is beneficial in a broad range of applications. Rapid near real-time determinations are found useful in areas such as air-toxic monitoring and evaluations at hazardous chemical dump sites. One application where speed is critical, is the detection and monitoring of chemical warfare agents. In such cases, it is advantageous to break the tradition of bringing the sample to the laboratory but, rather, bring the laboratory to the sample.

One of the choices of instrumentation for a mobile analytical laboratory is GC–AED. The AED provides positive confirmation of the presence of a given element by identifying its atomic fingerprint. This allows a peak in the chromatogram to be screened for arsenic, for example. The high sensitivity of the AED is also an advantage, since the compounds of interest are usually at trace levels. It has high selectivity which is essential for complex sample matrices. The AED can quantify Cl, S, P, and

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N in compounds commonly found in environmental samples [1]. It can selectively detect organometallic compounds containing Hg, Ni, Pb, Se, V, Fe, As, Sn, and Si [2, 3]. In fact, it can detect every element except helium.

The Hewlett-Packard 5921A Atomic Emission Detector along with the 5890 Series II Gas Chromatograph, 7673A Automatic Liquid Sampler and Chemstation comprise a system for the mobile analytical laboratory. Mobile operation, however, presents some additional problems for the instrumentation. Securing the instruments to the bench top is the first challenge. Determining how the hardware holds up to the shock and vibration of mobile use is an important issue.

2. The mobile analytical laboratory

The mobile analytical laboratory is manufactured by E-N-G Mobile Systems, Inc., 2245 Via de Mercados, Concord, CA 94520. A photograph is shown in Fig. 1. The laboratory measures 16 feet long and is equipped with two generators to provide electrical power for instruments and utilities. Electrical connections are provided for shore power operation when parked near a suitable outlet. A hydrogen generator is included along with a nitrogen generator capable of providing the necessary 2 l/min spectrometer purge required by the AED. The mobile analytical laboratory also

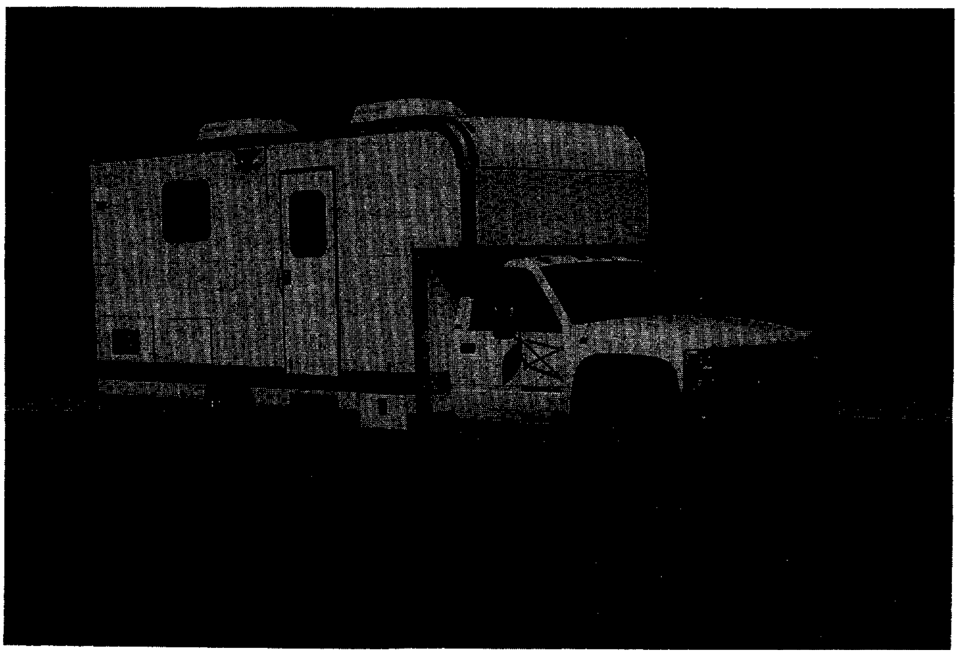

Fig. 1. External view of mobile analytical laboratory.

contains a fume hood, sink, refrigerator, chemical storage cabinet and a tank tray for bottled gasses. The counter top surface has a flush mounted hold down track similar to that used in aircraft. This provides a means to securely fasten instrumentation. The mobile analytical laboratory also has leveling jacks to stabilize and level the entire lab when in stationary operation. Although they were not used in our experiments, heated transfer lines are available for monitoring air toxic/hazardous compounds.

3. Installation and mounting hardware

The installation of the hardware was straightforward. A 5890A GC was attached to an interface plate which was bolted to the hold down track. The mechanical strength of the AED transporter assembly (this provides side-to-side motion of the AED to simplify column attachment) was increased by changing the guide wheels to a larger size. In addition, a brake was added that locked the AED firmly in place. Computer hardware was attached using sheet metal brackets that were bolted to the hold down channel. Rubber instrument feet were applied between the computer and the bracket to provide mechanical compliance and eliminate any motion. The computer monitor was held in place with a strap attached to the hold down channel. The computer keyboard was mounted in a drawer below the monitor. Fig. 2 shows the final hardware configuration.

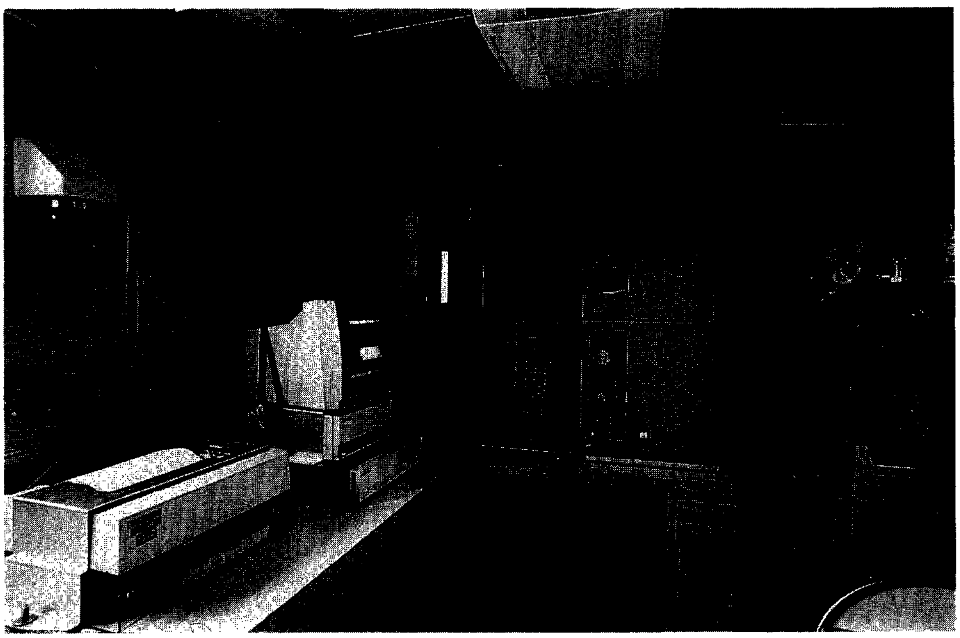

Fig. 2. View of GC–AED hardware mounting in mobile analytical laboratory.

TEST CONDITIONS

PERFORMANCE MEASURE	Standard Production Line Test	Mobile Lab Generators OFF	Mobile Lab Generators ON	Mobile Lab Tilted 2 Axes	Mobile Lab Chocks both IN and OUT	Mobile Lab Test After Rough Terrain	Mobile Lab Test During Temp Ramp
AED Checkout Sample	X	X	* X	* X	* X	* X	* X
AED Checkout MACRO	X	X	* X	* X	* X	* X	* X
Dark Current Noise	X	X	* X		* X	* X	

* Performed with generators ON.

Fig. 3. Mobile AED test matrix.

4. Initial testing

The initial objective was to subject the instrumentation to a variety of tests to screen for major problems. A test matrix was generated that documented AED performance from production line final test through a variety of vibration and thermal punishment. The test matrix is shown in Fig. 3. The criteria for each test was to achieve minimum detectable level (mdl) performance to the guaranteed specification level. In addition, actual mdls were also compared to that achieved in the production line final test.

The performance measure labeled AED Checkout Sample in Fig. 3 is a sequence of injections that provide for the measurement of minimum detectable level (mdl), chromatographic noise and peak area. This is performed on elements C, H, Cl, Br, D, S, N, Si, F, O and P. The sample is a mixture of measurement compounds in iso-octane as shown in Table 1.

The AED Checkout macro (Fig. 3) evaluates background levels of N, C, H and O. This macro also tests spectrometer UV throughput via the ratio of C193 to C165 line intensities. Signal to noise ratio of the He 706.5 nm spectral line is also done. Finally, a complete test of valving in the flow system is performed.

The measurement of Dark Current Noise of the photo diode array (PDA) was performed as indicated in Fig. 3. This is PDA output of a single photo diode for 300 consecutive readings at a 1 Hz data rate. Dark current noise is an excellent measure of the integrity of the AED light measuring system.

The test conditions presented the mobile GC–AED with a variety of abuse. The effect of generator vibration and tilt angle were the first examined. Effects of shipping chocks in the spectrometer was also tested. Complete checkout was performed after violent shake and vibration was administered by driving on a poor dirt road in a local park. This was to simulate traveling to a remote site and immediately running an analysis. Finally, effect of large temperature variation was simulated by shutting the

Table 1
HP 5921A atomic emission detector checkout sample composition and specification for minimum detectable level

Element and wavelength (nm)	mdl specification (pg/s)	Measurement compound
C 496	15	*t*-butyl disulfide
H 486	4	*t*-butyl disulfide
Cl 479	40	Trichlorobenzene
Br 478	60	Bromohexane
H 656	2	*t*-butyl disulfide
D 656	8	*n*-decane (perdeuterated)
C 193	1	*t*-butyl disulfide
S 181	2	*t*-butyl disulfide
N 174	50	Nitrobenzene
C 248	4	*t*-butyl disulfide
Si 252	85	Tetraethyl orthosilicate
F 690	80	Fluoroanisole
O 777	120	Nitrobenzene
P 178	1	Triethyl phosphate

vehicle's doors and windows and running the heaters while repeated injections were made.

4.1. Test results

The first observation was that the AED performance remained within specified levels throughout the entire test matrix. In fact, there was no measurable degradation whatsoever. Vibration from the generators and tilt angle had no effect on instrument performance. Vibration effects due to the presence or absence of the spectrometer shipping chocks was not observed. Violent shock from driving over rough terrain also had no discernible effect. Finally, an abrupt temperature change was applied to the GC–AED system. The temperature results are covered in a separate section later in the article.

Table 2 is a summary that shows a comparison of AED performance before and after all tests in Fig. 3 were performed. The data clearly indicate that the mdl performance of the AED was unaffected by the shock and vibration of rough terrain and 50 miles of typical paved road travel.

It needs to be pointed out that the mobile analytical laboratory was stationary during sample injection and analysis for all tests. Operation while in motion resulted in slightly higher noise and a corresponding increase of mdl. Although the mdl increase was small, it was enough to reduce the performance to just outside the guaranteed specification window. For those applications where full instrument performance is required, true mobile operation would not be recommended. Since many of the applications for this type of system would entail driving to the site, parking and performing the analysis, true mobile operation was not tested further.

Table 2
Comparison of mdl before and after completion of the test matrix shown in Fig. 3

Element and wavelength (nm)	mdl specification (pg/s)	mdl at production line final test (pg/s)	mdl after rough terrain + 50 miles (pg/s)
C 496	15	5.38	5.98
H 486	4	3.04	2.65
Cl 479	40	29.09	22.30
Br 478	60	42.18	36.13
H 656	2	0.32	0.20
D 656	8	2.11	1.90
C 193	1	0.32	0.31
S 181	2	0.93	0.74
N 174	50	6.07	3.90
C 248	4	2.40	2.82
Si 252	85	12.58	12.60
F 690	80	20.69	28.85
O 777	120	83.03	78.15
P 178	1	0.27	0.21

5. Road test

The experiments thus far were of a go/no go nature. Up to this point, the objective was to determine if there were any gross problems with the mobile AED. The pass/fail criteria compared performance to the guaranteed specifications of the instrument. Comparison at each test in the matrix was made to the performance achieved in production final test but the sample size was limited. At this time, a decision was made to increase the resolution of tests by gathering a statistically significant number of replicate tests which would allow comparison of before and after performance rather than referencing to the guaranteed specification. The experiment now was to identify if there was any significant change in performance after the AED was subjected to the conditions of mobile operation.

The map for this experiment is given in Table 3. There were three experimental conditions as shown in the first column. Condition 1 was the most benign (no generator vibration). Condition 2 examined the effect of generator vibration. Condition 3 used generator power, and after rough terrain was traveled. The three performance measures were mdl, chromatographic noise and peak area counts. Ten consecutive analyses were performed in each of the three conditions. Elemental analysis was done for the seven elements listed in Table 3. The same AED Checkout Sample was used but, in the interest of time, only the first two injections of the sequence were run.

Table 3
Experimental conditions to evaluate the effect of vibration caused by traveling on rough terrain

Conditions	Performance measures	Elements measured (nm)	Number of repetitions
(1) Shore power (generators OFF) Jacks up	mdl	C 193 N 174 S 181	
(2) Generators ON Jacks up	Chromatographic noise Area counts	C 496 H 486 Cl 479	10
(3) After rough terrain generators ON Jacks up		Br 478	

5.1. Test results

To analyze the data, significance tests were applied to compare Condition 1 vs. Condition 2 and Condition 1 vs. Condition 3, both essentially as separate experiments. The Condition 1 vs. Condition 3 analysis was the more important of the two. The comparison of sample means was made using a two sided *t*-test with a 95% confidence interval.

In general, there were no statistically significant changes between Condition 1 and Condition 3 with two exceptions. First, the mdl of N174 actually was better after being subjected to the vibration of Condition 3. Second, Condition 2 sample injection occurred under a temperature fluctuation. When the mobile analytical laboratory was entered to begin the test, it was uncomfortably hot and the temperature was adjusted down. The result of this was variation in peak area believed to be caused by thermal effects in the chromatographic flow system. The temperature coefficient of the pressure regulators were suspected. Nevertheless, the mdl levels were still within specification. Temperature effects of the GC–AED are covered in greater detail later in the article.

Graphically, the performance can be seen in Figs. 4–6 for mdl, chromatographic noise and area counts, respectively. It can be seen that mdl and noise track vary well both within a condition and between conditions. Area counts in Fig. 6 exhibited an additional effect visible in S181, C193 and CL479 plots. This was the thermal effect previously mentioned and is the focus of the next section. Overall, the performance of the AED showed no significant degradation caused by the shock and vibration of mobile application.

6. Effect of large temperature change

As previously mentioned, Condition 2 of the above experimental suite experienced the unplanned temperature variation during the analysis. The actual temperature

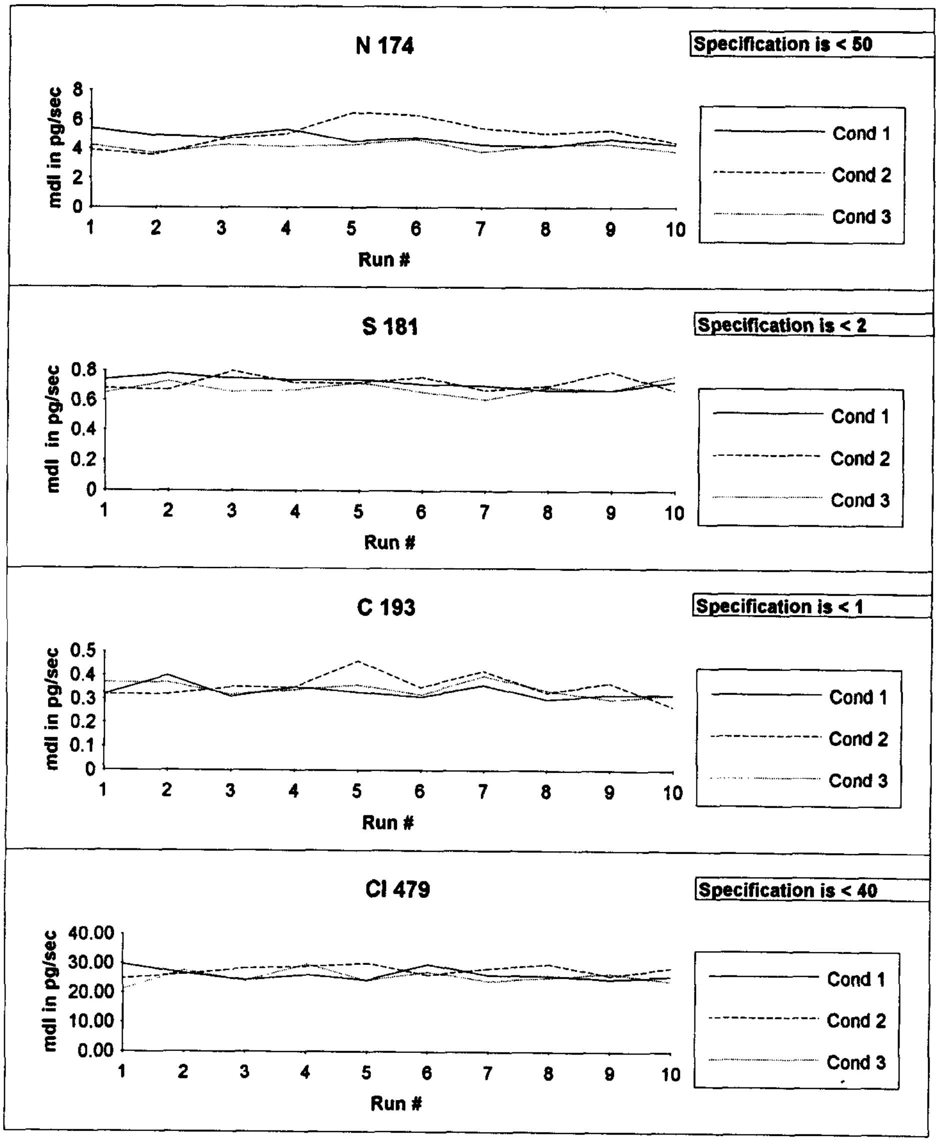

Fig. 4. Minimum detectable level for the three conditions of Table 3.

change was unknown so an experiment was designed to better quantify this effect. In field operation, it is possible for the mobile analytical laboratory doors to be opened during an analysis (and left open) or heat be turned on from a cold start. To simulate this, the experiment shown in Table 4 was devised. The test sample was the same as in the previous experiment. For both the temperature stable and temperature ramp

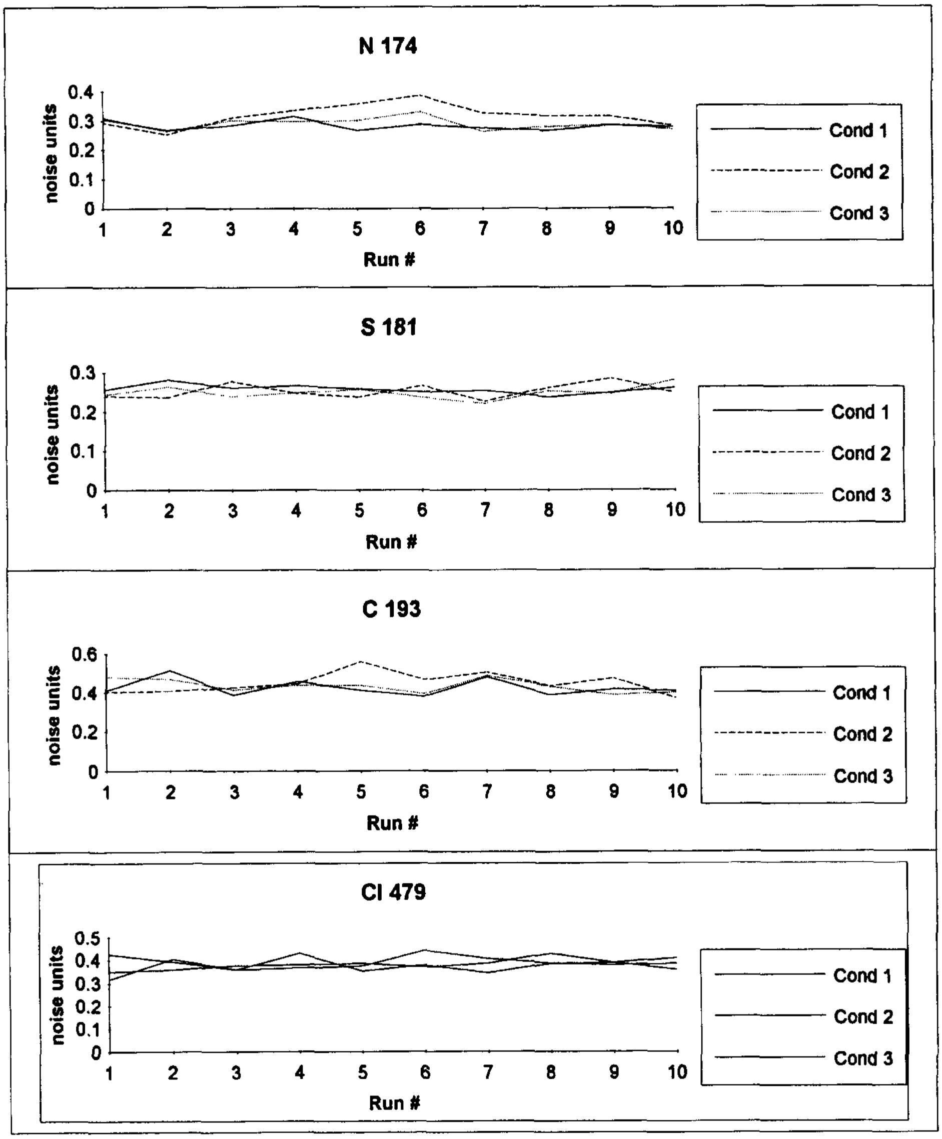

Fig. 5. Chromatographic noise for the three conditions of Table 3.

conditions, the three performance measures of mdl, chromatographic noise and area counts were measured for the seven elemental lines as shown. Ten consecutive runs, each about 12 min long, were analyzed. The temperature ramp was achieved by turning the mobile analytical laboratory's two heaters on from a cold start of approximately 5 °C to 27 °C over a period of about 1 h.

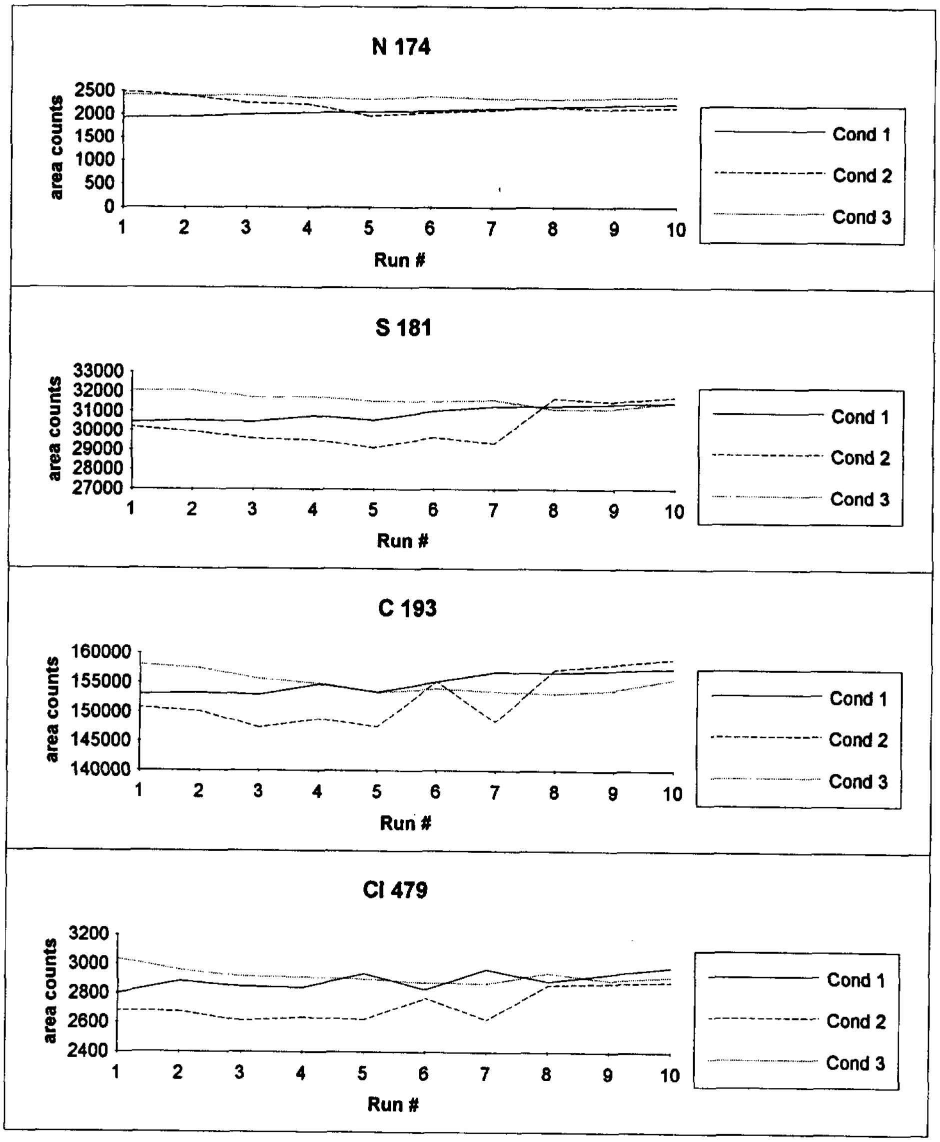

Fig. 6. Area counts for the three conditions of Table 3.

There was no measurable effect of this temperature ramp on mdl or chromatographic noise. Any real effect was masked by normal variation. There was, however, a small effect on peak area as shown in Fig. 7. There are two observations that can be made. First, the area counts for Condition A and Condition B are very similar. It must

Table 4
Test plan to measure the performance changes caused by large variation of ambient temperature

Test conditions	Performance measures	Elements measured (nm)	Number of repetitions
(A) Shore power			
Jacks up			
stable temperature	mdl	C 193	
		N 174	
(B) Generator power	Chromatographic noise	S 181	10
Jacks up		C 496	
stable temperature	Area counts	H 486	
		Cl 479	
(C) Generator power		Br 478	
Jacks up			
temperature ramp			

be mentioned that there was no closed loop temperature control system in the mobile analytical laboratory. Temperature was completely open loop and was adjusted via a control dial on the heater unit. Consequently, the temperature was not completely stable for Condition A and Condition B. It was estimated that the temperature variation during the analyses was approximately 3 °C.

The second observation is the change in peak area during the temperature ramp of Condition C. This is seen for all the elements measured and was believed to be caused by a flow related variation due to a pressure regulator temperature coefficient. The magnitude of this temperature coefficient for the C193 line, for example, is calculated to be about 0.4%/°C.

7. Conclusions

A comprehensive study of the feasibility of GC–AED in a mobile application was performed. No major problem in performance or ruggedness was observed. In fact, the performance of the system showed no statistically significant difference after driving down an unpaved road in order to simulate the shock and vibration expected in field use. The mounting hardware for the GC, AED and workstation components proved to be quite effective in keeping the hardware securely in place even during the adverse road conditions to which the system was subjected.

The effects of large temperature change was evaluated. Chromatographic noise and mdl showed no discernible effect. There was a small effect on area counts, however, in the order of 0.4%/°C for the C193 line. Methods that use internal standards can compensate for this effect but it is recommended that care be taken to avoid large temperature variation during an analysis. For maximum performance, optional thermostatted temperature control should be considered.

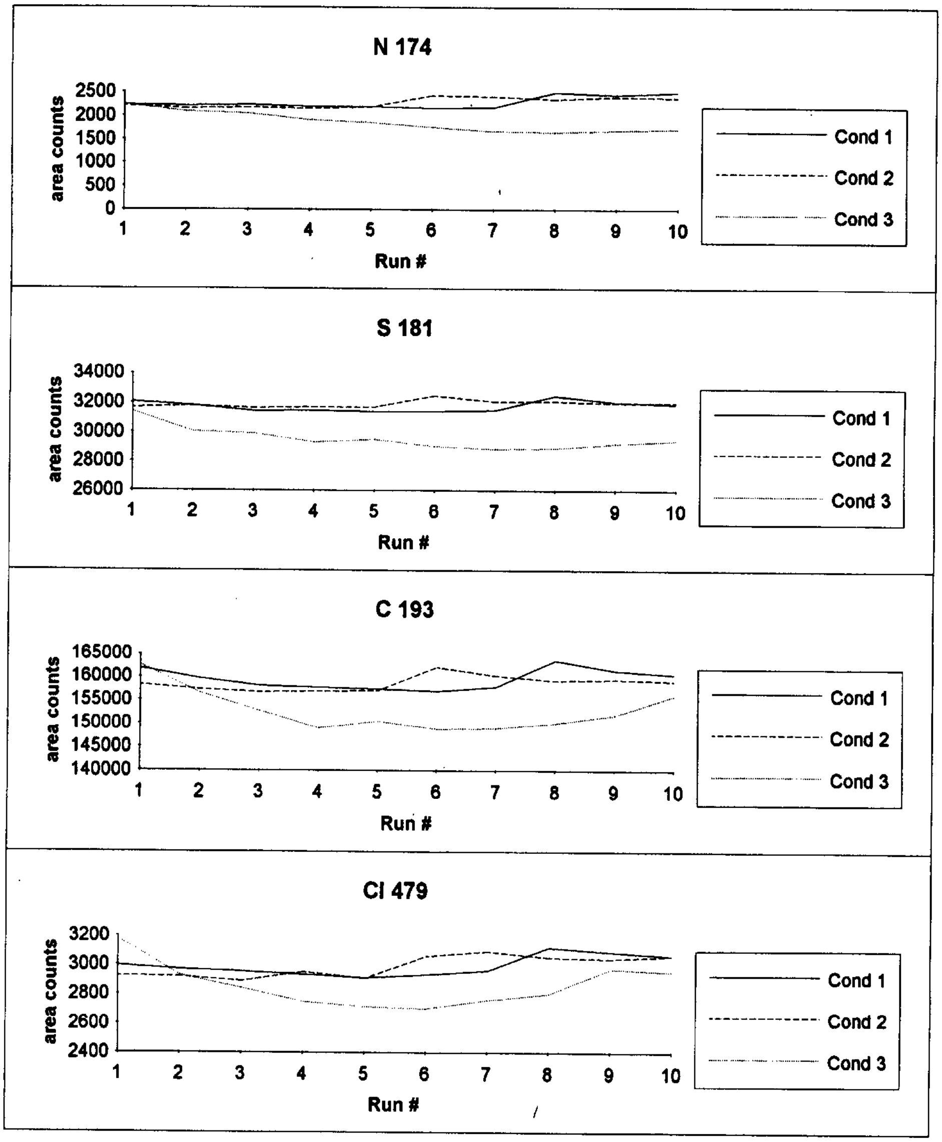

Fig. 7. Area counts for the three conditions of Table 4.

Finally, true mobile operation (performing an analysis while in motion) resulted in a slightly higher noise level. This caused an increase in the minimum detectable levels to just outside the specification window. It is recommended that the "park and inject" technique be used when possible.

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