Talanta 95 (2012) 36–41

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Evaluation of compound-independent calibration using gas chromatography with atomic emission detection

Gang Li[a,b], Da Wu[b], Wenyan Xie[b], Xiangmin Zhang[a,*], Baizhan Liu[b,**]

[a] Department of Chemistry, Fudan University, 200433, Shanghai, PR China
[b] Technology Center, Shanghai Tobacco Group Co., Ltd, 200082, Shanghai, PR China

ARTICLE INFO

*Article history:*
Received 11 January 2012
Received in revised form 9 March 2012
Accepted 22 March 2012
Available online 29 March 2012

*Keywords:*
Atomic-emission detection
Inter-elements response factor ratios
Raw-formula determination

ABSTRACT

The evaluation of compound-independent calibration (CIC) using gas chromatography (GC) with atomic emission detection (AED) is demonstrated by the identification of several sulfur or nitrogen compounds. Among other GC detectors, the advantage of using the AED is the selectivity of detection. Because contradictory results have been reported for the determination of numeric atomic ratios of elements, we set up a study with the objectives not only of applying these techniques but of determining under which conditions they will yield satisfactory results. The column pressure dependence of AED response is demonstrated through studies performed with constant pressure of 20, 30, and 40 psi. Moreover, the data collected in this study are evidence that inter-elements response factor ratios, particularly for the C/S, is very dependent on the molecular mass and concentration of the chemicals analysed whereas molecular structure seems to have less effect on the AED signal. We therefore suggest the use of a reference set of compounds covering a large chromatographic window, which enables the selection, within this set, of the most appropriate reference compound for calibration and for determination of the raw formula of an unknown analyte.



## 1. Introduction

Gas chromatography (GC) is widely used for the separation of mixtures. Many selective and sensitive detectors have been developed which are useful for qualitative and quantitative determination of sample components [1–4]. Quantification of individual sample components requires determination of the detector response factor for each compound of interest. Typically, this is achieved by producing calibration curves using standard solutions having known concentrations of each component. Practically, however, this is not always a viable approach, e.g., when the analytes are toxic, carcinogenic, mutagenic, or environmentally hazardous, or when standards for the compounds of interest simply are not available.

Compound-independent calibration (CIC), the use of a single compound to quantify other components present in the sample, is an attractive alternative which could potentially eliminate these problems, as well as speed up analyses by reducing standard preparation and analysis time [5–7]. One technique to which CIC can theoretically be applied is gas chromatography (GC) with microwave-induced plasma atomic emission detection (AED) [8–10]. Its principle was described by McCormack et al. [11] and has been marketed by Hewlett–Packard. Briefly, this detector uses microwave-induced plasma in which molecules eluting from the chromatographic system are atomised in excited states; relaxation of excited atoms results in emission of photons at characteristic wavelengths which are, in turn, detected by means of a spectrometer. The ability to detect specific-element-containing components while discriminating any other possible complications is the key point of this effective detection. Virtually all atoms are detectable by AED, albeit with very different limits of detection. Unfortunately, numerous factors can affect the AED response at any particular wavelength [12,13]. Among these are the nature and concentration of reagent gases in the plasma, the flow rate of makeup gas into the detector and the presence of very large concentrations of carbon containing species in the plasma. Unlike the mass spectrometric detection, the AED does not have direct identification capability for the compound structure. However, the AED can still be used as an identification tool by a peak pattern recognition approach. An important advantage of the GC–AED systems appears to be the possibility of a highly selective registration of target elements in molecules of the components [14–17]. Depending on the specific atomic emission lines chosen, the AED will detect the components, which

* Corresponding author. Tel.: +86 21 65643983; fax: +86 21 65643983.
** Corresponding author. Tel.: +86 21 65649403; fax: +86 21 61669950.
*E-mail addresses:* xminzhang@fudan.edu.cn (X. Zhang), Liubz@sh.tobacco.com.cn (B. Liu).

0039-9140/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.03.044

contain the specific element of interest (such as nitrogen or sulfur).

Due to the complexity of the detector, it is not surprising that the literature contains conflicting reports concerning the compound independence of AED response. Some studies support the concept of CIC with the GC–AED [18,19], while others indicate an apparent dependence of AED response on compound structure [20–22]. This suggests the effects could depend on concentration, molecular mass, and structural features of the chemicals analysed. However, the potential of AED for CIC is of still particular interest, because standards may not always be available or because avoiding the manipulation of highly toxic chemicals is desirable when possible.

In view of this, the major goal of the present work is to evaluate CIC using the GC–AED technique. In order to understand more precisely the factors determining the feasibility of CIC and raw-formula determination, we undertake a comprehensive study to determine carbon-to-hydrogen (C/H), carbon-to-nitrogen (C/N), and carbon-to-sulfur (C/S) response ratios for several nitrogen or sulfur-containing compounds. Effects of different factors (column head pressure, molecular structure, concentration of analytes, and molecular mass) on the performance of CIC using GC–AED technique are thoroughly discussed.

## 2. Experimental

### 2.1. Instrumentation

All analyses were performed with GC-AED coupled with Deans switching devices and this technique was reported by our research group [23]. Briefly, a 7890 Series gas chromatograph (Agilent Technologies, USA) hyphenated to a G2350A atomic-emission detector (Joint analytical systems, GmbH, Germany). The GC was equipped with a split/splitless inlet and a capillary flow technology based Deans switching system (Agilent Technologies, USA). The primary and the second columns were both 30 m × 0.25 mm I.D. × 0.25 μm HP-5 installed in the GC oven. A restrictor, (3 m × 180 μm I.D. deactivated fused silica), was connected between the second output of the Deans switch and a monitoring flame ionisation detector. A VICI Model I-23572-HP2 (USA) helium purifier was used inline between the helium tank and the plasma cavity.

### 2.2. Reagents

Analytical standards used for universal calibration were nitrogen-containing compounds, 1-pentylamine, heptylamine, nonylamine, n-undecylamine, tridecylamine and tetradecylamine, and sulfur-containing compounds, 1-pentanethiol, 1-octanethiol, 1-nonanethiol, 1-undecanethiol, 1-tetradecanethiol, 1-pentadecanethiol, cyclopentanethiol, thioanisole, and 1,2-benzenedithiol. Application of the methodology implemented was performed with ethyl disulfide, dipropyl disulfide, dibutyl disulfide, cyclopentanethiol, thioanisole, 1,2-benzenedithiol, myosmine and anabasine. All of them were used as received from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Tert-butyl methyl ether used as solvents from Merck (Darmstadt, Germany) was of analytical grade quality. It was used without further purification.

Caution! Some of the chemicals used in this study, especially myosmine and anabasine are highly toxic agents which should be manipulated only by experienced staff under proper safety conditions.

### 2.3. Sample preparation

Standard solutions of nitrogen-and sulfur-containing compounds were prepared in tert-butyl methyl ether and stored in the refrigerator at 2–4 °C. For calibration experiments these mixture solutions were diluted stepwise with the same solvent to concentrations suitable for GC analysis. To accurately subtract carbon background from the nitrogen and sulfur signals, at least one component of the solution had to be a carbon-containing compound that did not contain nitrogen or sulfur. Thus, each standard solution also contained 2-hexanone at a concentration comparable to the amine and thiol series. The nitrogen and sulfur background amount was set by suppressing the 2-hexanone peak in each chromatogram. Each data point on the calibration plots represented the average peak area from five replicate injections.

### 2.4. GC conditions

The carrier gas was helium (99.9999% purity). All injections were 1 μL in volume. The splitless injector was maintained at 280 °C. The GC oven temperature was held at 45 °C for 1 min and then was taken to 280 °C at 15 °C $min^{-1}$, where the temperature was held for 4 min.

### 2.5. AED conditions

Transfer line and cavity block were both maintained at 280 °C. In order to vent the solvent before entering the plasma and prevent carbonaceous deposition on the wall of the discharge tube, the analyses were carried out on the GC–AED coupled with Deans switching device combination [23]. The detector was operated at emissions wavelengths of 193 nm for carbon, 174 nm for nitrogen, 181 nm for sulfur, and 486 nm for hydrogen, with reagent gases recommended by the manufacturer (Shanghai No.5 Steel Works, Shanghai, China). According to the closeness of carbon, nitrogen and sulfur lines, the three elements were monitored by the diode array during the same analytical run. Helium flow through the cavity was set to 60 mL $min^{-1}$ and the scavenger gases were hydrogen and oxygen at 11.5 and 21 psi, respectively. The spectrometer was purged with nitrogen at 400 mL $min^{-1}$. Filter and back amount adjustments were set according to the default specifications.

### 2.6. Procedures

Inter-element response factor ratios were calculated from the average peak area for each compound by use of Eq. (1), where C, X and C/X were carbon, any element other than carbon (hydrogen, nitrogen, or sulfur) and the inter-element response factor ratios, respectively [24]. C-area and X-area were the chromatographic peak areas from the chromatograms of an element X. C-moles and X-moles was the number of moles of an element C and X in a given compound.

$$\frac{C}{X} = \frac{C_{area}}{X_{area}} \times \frac{X_{moles}}{C_{moles}} \quad (1)$$

The number of atoms of an element X in an unknown compound could theoretically be determined from a reference element ratio by use of Eq. (2), where $X_u$ was the number of atoms of an element X and $C_u$ was the number of atoms of an element C in an unknown compound.

$$Xu = \frac{C_{area,\,unknown}}{C_{area,\,known}} \times \frac{X_{area,\,unknown}}{X_{area,\,known}} \times \frac{X_{moles,\,known}}{C_{moles,\,known}} \times C_u \quad (2)$$

Eq. (3) could also easily provide the number of carbon atoms in an unknown compound.

$$Cu = \frac{C_{area,\,known}}{C_{area,\,unknown}} \times \frac{X_{area,\,known}}{X_{area,\,unknown}} \times \frac{C_{moles,\,known}}{X_{moles,\,known}} \quad (3)$$

This principle was used for determination of C/H, C/N and C/S ratios to obtain partial empirical formulae for the compounds. The maximal precision of the determination of the C/X ratios was attained

**Table 1**
Comparison of AED response factor using various column flow conditions.

| Constant pressure (psi) | ERF[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C (193 nm) | | | H (486 nm) | | | S (181 nm) | | |
| | Range[b] | Average[c] | RSD[d] | Range | Average | RSD | Range | Average | RSD |
| 20 | 283–337 | 301 | 4.1 | 11–31 | 20 | 16 | 48–145 | 93 | 4.6 |
| 30 | 400–447 | 402 | 3.2 | 121–170 | 136 | 4.4 | 63–175 | 110 | 3.3 |
| 40 | 325–401 | 337 | 3.3 | 108–169 | 125 | 3.4 | 54–140 | 91 | 2.6 |

[a] Elemental response factor, peak area per nanogram of element injected.
[b] Minimum and maximum values of the ERFs for the 12 compounds (1-pentanethiol, 1-octanethiol, 1-nonanethiol, 1-undecanethiol, 1-tetradecanethiol, 1-pentadecanethiol, ethyl disulfide, dipropyl disulfide, dibutyl disulfide, cyclopentanethiol, thioanisole and 1,2-benzenedithiol).
[c] Average of the ERFs for the 12compounds.
[d] Relative standard deviation of the ERFs for the 12 compounds.

only if the chromatograms in the carbon and the element's channels were recorded simultaneously, and the selectivity was rather high, so the presence of other elements did not affect the signals for carbon and the other element. Owing to the low sensitivity of AED for oxygen calibration on this element was not extensively studied; calculations were, however, performed where possible using the CIC module of the instrument.

## 3. Results and discussion

### 3.1. Column flow conditions

The relationship between elemental response factor (ERF, peak area per nanogram of element injected) [25] and column pressure was studied in this work. Constant column head pressure of 20, 30, and 40 psi were investigated. Table 1 showed the results from these experiments for three detection wavelengths. For each column head pressure and detection wavelength studied, the ERFs for the compounds were generally consistent, with relative standard deviations (RSDs) of 5% or less, except for the element of hydrogen (20 psi) where RSD values increased to 16%. This indicated that the AED response was independent of the compound structure under these conditions except for hydrogen at low pressure. ERF values did, however, depend on the column pressure used. The lowest average ERF was observed with a pressure of 20 psi for all three elements considered. Increasing the pressure to 30 psi caused an increase in the average ERF for each element. This was likely due to a small increase in the residence time of each element in the plasma. However, when the pressure was increased to 40 psi, the average was decreased. This effect was probably due to both a decrease in peak width (i.e., more response per unit time) and a change in the compound interactions within the plasma [26,27]. Therefore, it was extremely important when data from different experiments were compared to ensure that all were collected at the same column head pressure.

### 3.2. Effect of analyte concentration

Inter-element response factor ratios were determined using six amines compounds, alkyl chains with 5, 7, 9, 11, 13 and 14 carbon atoms and six sulfur-containing compounds, alkyl chains with 5, 8, 9, 11, 14 and 15 carbon atoms, for amounts in the range 5–100 ng of compound injected.

To assess the effect of concentration on response factors, linear regression curves for each inter-element ratio (C/H, C/N and C/S) versus analyte concentration were plotted for each compound and the resulting slope values were compared with a null slope $P_0 = 0$ (which should be observed if concentration had no effect) using Student's *t*-test [28]. Experimental *t* values are calculated according to the formula:

$$t = \frac{p - p_0}{SE_p},$$

where $P$ was the experimental slope for the analyte of interest, $P_0$ was the null slope ($P_0 = 0$), and $SE_p$ was the standard error associated with the experimental slope $P$. The values reported in Table 2, were compared with reference *t* values for a level of confidence of 95% ($P < 0.05$) to verify a significant deviation between $P$ and $P_0$.

These results showed that C/N and C/S response factors significantly depended on analyte concentration. On the other hand, no significant dependence on C/H ratio was observed. More generally, the effect of concentration was more pronounced for the nitrogen and sulfur lines, for which concentrations were more important. This was probably because of an increase in the amount in the plasma, leading to loss of energy owing to extensive chemical interactions between nitrogen or sulfur compounds and walls of the discharge tube. Such interactions had previously been invoked as being responsible for poor determinations of C/F ratios [29]. Another possibility was that larger amounts of molecules eluted in the plasma result in reduced atomisation yields, and thus to a lower AED signal [17,30].

Molecular formula for 1-octanethiol at 11 $\mu g\,mL^{-1}$ were obtained using as reference the same compound at different concentrations (Table 3). It seemed that the percent deviations between theoretical and calculated atoms for 1-octanethiol were carbon, 0–5%; hydrogen, 0–5.3%; and sulfur, 0–6.1%, when the concentration of the reference compound was close to that of the 'unknown' compound. When concentration increased to 55 $\mu g\,mL^{-1}$, however, deviations could increase to 15% for carbon-number determination. These results were evidence of the importance of using reference compounds at comparable element concentration to those of the compounds being characterised, to obtain better accuracy. In practice, as far as we known, the size of the peak was proportional to the concentration of the analyte. By comparing the areas of the chromatographic peaks for both the sample and a standard containing a known concentration of the analyte, we could evaluate the concentration of the analyte in the sample.

### 3.3. Effect of molecular weight

The effect of molecular weight (MW) on inter-element response factor ratios was also studied for six amines compounds, alkyl chains with 5, 7, 9, 11, 13 and 14 carbon atoms and six sulfur-containing compounds, alkyl chains with 5, 8, 9, 11, 14 and 15 carbon atoms.

Average C/H, C/N, and C/S response factor ratios resulting from triplicate injections of nitrogen-and sulfur-containing compounds solutions with different element concentrations were calculated

**Table 2**
Experimental values of *t* indicating the dependence of C/H, C/N, and C/S ratios on analyte concentration.

| | Amines (t = 2.26) | | | | | |
|---|---|---|---|---|---|---|
| | C5 | C7 | C9 | C11 | C13 | C14 |
| *t* value for C/H ratio determination | 0.43 | 0.34 | 0.96 | 0.80 | 1.06 | 1.59 |
| *t* value for C/N ratio determination | 2.29* | 2.70* | 3.33* | 4.58* | 6.32* | 7.45* |
| | Thiols (*t* = 2.18) | | | | | |
| | C5 | C8 | C9 | C11 | C14 | C15 |
| *t* value for C/H ratio determination | 0.69 | 0.13 | 0.75 | 1.12 | 1.15 | 2.23* |
| *t* value for C/S ratio determination | 8.48* | 9.3* | 10.4* | 11.0* | 10.7* | 10.3* |

* $P < 0.05$ – see text for details.

**Table 3**
CIC calculations for 1-Octanethiol using the compound itself as reference.

| | Concentration ($\mu g\,mL^{-1}$) | Number of C | D[a] % | Number of H | D% | Number of S | D% |
|---|---|---|---|---|---|---|---|
| 1-Octanethiol | 5.5 | 8.3 | 3.8 | 18 | 3.0 | 0.97 | 2.8 |
| $C_8H_{18}S$ | 11 | 8.0 | 0 | 18 | 0 | 1.0 | 0 |
| | 22 | 8.4 | 5 | 19 | 5.3 | 0.94 | 6.1 |
| | 55 | 9.2 | 15 | 20 | 13 | 1.1 | 11 |

[a] The percent deviations between theoretical and calculated atoms for 1-octanethiol.

for each compound (Table 4). The results showed a decrease of C/S inter-element response factor ratio with increasing MW, but revealed that C/H response factor ratio and C/N response factor are independent of MW. The effect of MW on C/S response factor ratio might be partly explained by increased tailing of the sulfur peak for high molecular mass compounds leading to lower accuracy of integration and probably loss of sensitivity or an incomplete fragmentation of high molecular weight compounds inside the plasma.

Thus, to further illustrate the effect of MW on C/S response factor ratios, the formulae of three volatile sulfur compounds, ethyl disulfide, dipropyl disulfide and dibutyl disulfide were determined, using as references six thiols, alkyl chains with 5, 8, 9, 11, 14 and 15 carbon atoms, respectively. The results confirmed that references with close MW should be used for partial accurate determination of sulfur-containing compounds. Fig. 1 showed the percent deviation of calculated vs. actual number of carbon atoms in the raw formula, plotted versus the difference between the MW between each thiol and the reference compound chosen for calibration. This plot gave evidence of significant variation in carbon number accuracy depending on the MW of reference compound. It might, however, be noted that using a lighter compound as calibration reference usually yields acceptable results whereas heavier compounds gave rise to large errors.

**Table 4**
Effect of molecular weights on inter-element response factors.

| | | | Inter-elements response factors | |
|---|---|---|---|---|
| Amines | Raw-formula | Mw | C/H | C/N |
| 1-Pentylamine | $C_5H_{13}N$ | 87 | 2.35 | 45.6 |
| Heptylamine | $C_7H_{17}N$ | 115 | 2.47 | 40.5 |
| Nonylamine | $C_9H_{21}N$ | 143 | 2.41 | 47.7 |
| n-Undecylamine | $C_{11}H_{25}N$ | 171 | 2.66 | 43.8 |
| Tridecylamine | $C_{13}H_{29}N$ | 199 | 2.81 | 46.1 |
| Tetradecylamine | $C_{14}H_{31}N$ | 213 | 2.77 | 44.7 |
| Thiols | Raw-formula | Mw | C/H | C/S |
| 1-Pentanethiol | $C_5H_{12}S$ | 104 | 2.63 | 7.10 |
| 1-Octanethiol | $C_8H_{18}S$ | 146 | 2.96 | 5.15 |
| 1-Nonanethiol | $C_9H_{20}S$ | 160 | 2.87 | 4.86 |
| 1-Undecanethiol | $C_{11}H_{24}S$ | 188 | 2.45 | 3.92 |
| 1-Tetradecanethiol | $C_{14}H_{30}S$ | 230 | 2.87 | 2.45 |
| 1-Pentadecanethiol | $C_{15}H_{32}S$ | 244 | 2.78 | 2.28 |

### 3.4. Applications

Alkaloid was generally acknowledged to be the principal agent motivating tobacco smoking and the main impediment to cessation [31]. Volatile sulfur compounds (VSC) exhibited in general intense smelling properties due to their extremely low odour thresholds [32]. Depending on their levels in beverages and foods, they contributed favourably to the aroma or to off-flavour. Thus, after this series of systematic investigations, we attempted to determine, by GC–AED analysis, the raw formulae of two alkaloid agents (myosmine and anabasine) and the aliphatic and aromatic VSCs (ethyl disulfide, dipropyl disulfide, dibutyl disulfide, cyclopentanethiol, thioanisole and 1,2-benzenedithiol).

In practice, when analysing unknown chemicals for which, by definition, molecular weight was unknown, retention time could be use as an alternative property for selecting a reference, assuming that retention time was at least partly correlated to MW. Alternatively, GC–MS detection might be used in parallel to afford useful MW data.

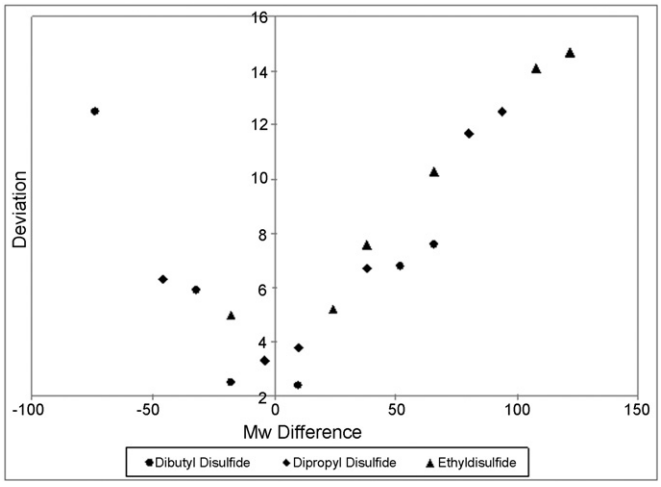


**Fig. 1.** Percent deviation in experimental carbon number values versus difference between the molecular weight of the interest of volatile sulfur compounds and that of the thiols with the different alkyl chains used as reference (all chemicals injected as 11 $\mu g\,mL^{-1}$ solutions in tert-butyl methyl ether).

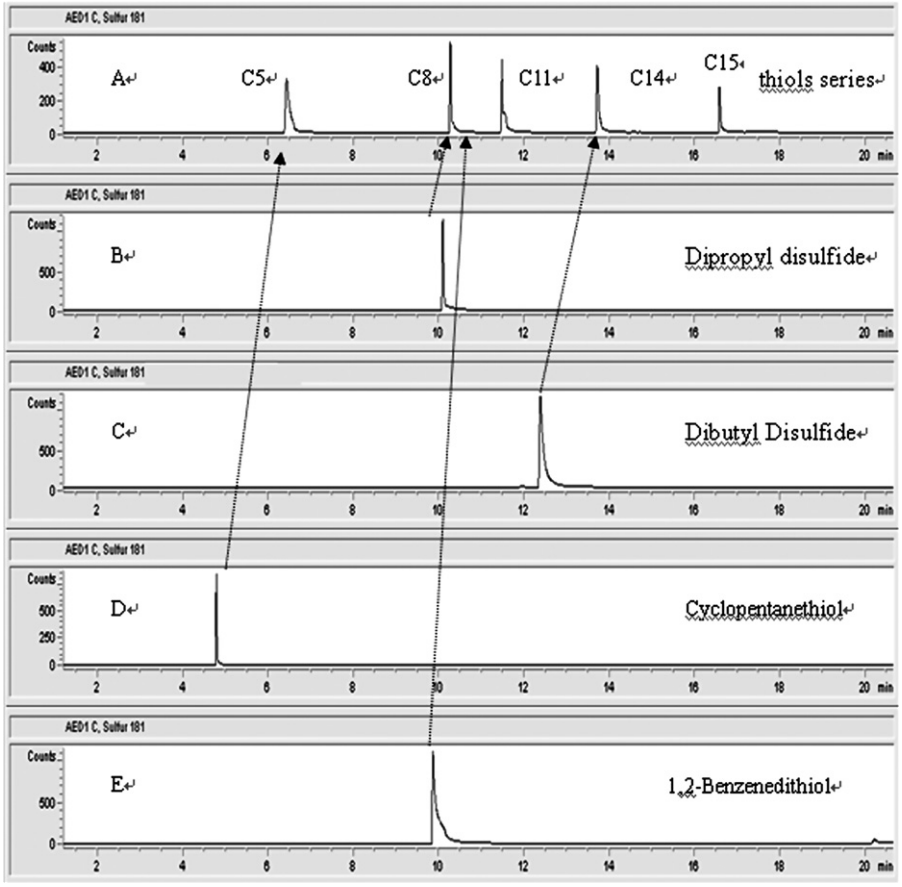


**Fig. 2.** GC-AED chromatograms obtained after injection of (A) five members of the thiols series, (B) dipropyl disulfide, (C) dibutyl disulfide, (D) cyclopentanethiol and (E) 1,2-benzenedithiol (each 22 $\mu g\,mL^{-1}$ in tert-butyl methyl ether). Dashed lines indicate the reference compound chosen for calibration of each analyte of interest.

**Table 5**
Empirical formula determination for the interest compounds.

| Compound | Reference | Raw formula | Calculated formula |
|---|---|---|---|
| Ethyl disulfide | 1-Pentanethiol | $C_4H_{10}S_2$ | $C_{4.2}H_{10.3}S_{2.07}$ |
| Dipropyl disulfide | 1-Octanethiol | $C_6H_{14}S_2$ | $C_{5.8}H_{14.4}S_{2.08}$ |
| Dibutyl disulfide | 1-Undecanethiol | $C_8H_{18}S_2$ | $C_{8.2}H_{19}S_{2.1}$ |
| Cyclopentanethiol | 1-Pentanethiol | $C_5H_{10}S$ | $C_{5.2}H_{10.4}S_{1.06}$ |
| 1,2-Benzenedithiol | 1-Octanethiol | $C_6H_6S_2$ | $C_{6.3}H_{6.5}S_{2.1}$ |
| Myosmine | Nonylamine | $C_9H_{10}N_2$ | $C_{9.3}H_{10.4}N_{2.06}$ |
| Anabasine | n-Undecylamine | $C_{10}H_{14}N_2$ | $C_{10.5}H_{13.4}N_{2.08}$ |

In this experiment, formula calculation was performed with the CIC module, using as reference the thiols with the retention time closest to that of the interest being characterised (Fig. 2). The theoretical and calculated formula were shown in Table 5. The results showed relatively low deviation for carbon (2.5–5%), hydrogen (2.9–5.6%), nitrogen (less than 4%) and sulfur (less than 6%). This also indicated that calibration should be performed with a compound of similar concentration level and with a comparable mass or a retention time comparable with that of the unknown analyte being characterised, even those with very different molecular structures.

## 4. Conclusions

Extensive study of AED response in GC–AED analysis of amines, thiols, and other interest compounds, under different conditions, enabled assessment of the effect of GC column head pressure, sample concentration, and analyte molecular mass on inter-element response factor ratio. The column head pressure had a pronounced effect on the AED ERF. Concentration and molecular mass of the analyte seemed to be prominent factors determining the compound-dependence of AED response. Variations of element response factors might be correlated both with chromatographic phenomena and with alteration of the atomisation process.

After this series of systematic investigations, the main conclusion drawn from these results was that calibration should be performed with a compound of similar concentration level and with a comparable mass or, when this could not be achieved, a retention time comparable with that of the unknown analyte being characterised. The proposed strategy was to use a mixture of reference compounds at appropriate concentrations covering the whole chromatogram, from which could be extracted the most suitable compound for calibration of an unknown analyte.

## Acknowledgements

The authors are grateful to Science and Technology Commission of Shanghai (Grant No. 11R21422000) for financial support.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.talanta.2012.03.044.

## References

[1] C. Mardones, D.V. Baer, J. Silva, M.J. Retamal, J. Chromatogr. A 1215 (2008) 1–7.
[2] J.S. Chiang, S.D. Huang, Talanta 71 (2007) 882–886.

[3] Y. Cristina, B. Susana, C. Pilar, L. Regina, P.A. Consuelo, H. Antonio, A. Agustín, J. Agric. Food Chem. 53 (2005) 5105–5109.
[4] Y. Li, T. Pang, Z.M. Guo, Y.L. Li, X.L. Wang, J.H. Deng, K.J. Zhong, X. Lu, G.W. Xu, Talanta 81 (2010) 650–656.
[5] J.J. Johnston, D.A. Goldade, D.J. Kohler, J.L. Cummings, Environ. Sci. Technol. 34 (2000) 1856–1861.
[6] A. González-Gago, J.M. Marchante-Gayón, J.I.G. Alonso, J. Anal. At. Spectrom. 22 (2007) 1138–1144.
[7] A. Sola-Vazquez, J.M. Costa-Fernandez, R. Pereiro, A. Sanz-Medel, Anal. Bioanal. Chem. 401 (2011) 2771–2777.
[8] J.T. Anderson, Anal. Bioanal.Chem. 373 (2002) 344–355.
[9] S.C. Diaz, J.R. Encinar, A. Sanz-Medel, J.I.G. Alonso, Anal. Chem. 82 (2010) 6862–6869.
[10] V.M. Carin, K. Weeraya, A.Z. Claudia, B.C. Elina, J.M. Philip, J. Sep. Sci. 29 (2006) 1909–1921.
[11] A.J. McCormack, S.G. Tong, W.D. Cooke, Anal. Chem. 37 (1965) 1470–1476.
[12] N.A. Stevens, M.F. Borgerding, Anal. Chem. 71 (1999) 1083–1086.
[13] K.D. Bartle, S.R. Hall, K. Holden, S.C. Mitchell, A.B. Ross, Fuel 88 (2009) 348–353.
[14] L. Elci, N. Kolbe, S.G. Elci, J.T. Anderson, Talanta 85 (2011) 551–555.
[15] P. Canosa, R. Montes, J.P. Lamas, M. García-López, I. Orriols, I. Rodríguez, Talanta 79 (2009) 598–602.
[16] N. Campillo, R. Peñalver, I. López-García, M. Hernández-Córdoba, J. Chromatogr. A 1216 (2009) 6735–6740.
[17] G.A. Zachariadis, E. Rosenberg, Talanta 78 (2009) 570–576.
[18] W. Elbast, M.S. Caubet, D. Deruaz, J.L. Brazier, Anal. Lett. 32 (1999) 1627–1641.
[19] A. Johnson, N. Olson, Arch. Environ. Contam. Toxicol. 41 (2001) 339–344.
[20] A.M. González, P.C. Uden, J. Chromatogr. A 898 (2000) 201–210.
[21] E.S. Chernetsova, A. Revelsky, D. Durst, T.G. Sobolevsky, I.A. Revelsky, Anal. Bioanal. Chem. 382 (2005) 448–451.
[22] E.S. Chernetsova, A.I. Revel'skii, I.A. Revel'skii, Y.A. Zolotov, J. Anal. Chem. 65 (2010) 770–784.
[23] G. Li, D. Wu, Y. Wang, W.Y. Xie, X.M. Zhang, B.Z. Liu, J. Sep. Sci. 35 (2012) 334–340.
[24] K. Łaniewski, M. Vågerö, E. Forsberg, T. Forngren, G. Hagman, J. Chromatogr. A 1027 (2004) 93–102.
[25] N.A. Stevens, M.F. Borgerding, Anal. Chem. 70 (1998) 4223–4227.
[26] K. Janak, A. Colmsjo, C. Ostman, J. Chromatogr. Sci. 33 (1995) 611–621.
[27] F. Augusto, A.L.P. Valente, J. Chromatogr. A 819 (1998) 85–91.
[28] M. Tubino, R.L.D. Souza, Talanta 68 (2006) 776–780.
[29] N.R. Hardas, P.C. Uden, J. Chromatogr. A 844 (1999) 271–281.
[30] G.A. Zachariadis, E. Rosenberg, J. Chromatogr. B 877 (2009) 1140–1144.
[31] S.R. Sousa, S.E. Bialkowski, Anal. Chim. Acta 433 (2001) 181–186.
[32] T.E. Siebert, M.R. Solomon, A.P. Pollnitz, D.W. Jeffery, J. Agric. Food Chem. 58 (2010) 9454–9462.