

Article

## Development of a Combined Real Time Monitoring and Integration Analysis System for Volatile Organic Compounds (VOCs)

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**Abstract:** A combined integration analysis and real time monitoring (Peak Capture System) system was developed for volatile organic compounds (VOCs). Individual integration analysis and real time monitoring can be used to qualitatively and quantitatively analyze VOCs in the atmosphere and in indoor environments and determine the variation in total VOC (TVOC) concentration with time, respectively. In the Peak Capture System, real time monitoring was used to predict future elevations in the TVOC concentration (peak), and this was used as an indicator of when to collect (capture) ambient air samples for integration analysis. This enabled qualitative and quantitative analysis of VOCs when the TVOC concentration was high. We developed an algorithm to predict variation in the TVOC concentration, and constructed an automatic system to initiate air sampling for integration analysis. With the system, auto-sampling and analysis of VOCs in a conventional house were conducted. In comparison with background concentrations, the

results of peak analysis enabled identification of compounds whose concentration rose. This also enabled an evaluation of possible VOC emission sources.

**Keywords:** volatile organic compounds (VOCs); integration analysis; real time monitoring; peak capture system

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## 1. Introduction

Volatile organic compounds (VOCs) are organic compounds with large vapor pressures, and include aldehydes, ketones, and other light hydrocarbons. VOCs can cause irritation, and they can also negatively affect human health at relatively high concentrations [1]. Possible side effects of exposure to VOCs include sick building syndrome (SBS) or multiple chemical sensitivity (MCS), which can occur even at low concentrations [2]. To investigate the contribution of VOCs to these illnesses and to maintain air quality, the composition of VOCs in the air needs to be determined.

The various methods for measurement of VOCs in air can be divided into three classes according to the amount of measurement work involved and the degree of information they provide [3]. These classes are: direct-reading instruments, no identification, and identification of individual compounds. Measurement of VOCs can be conducted by integration analysis and real time monitoring, which are classed as identification of individual compounds and direct-reading instruments, respectively. In integration analysis, VOCs are collected into a sorbent tube with an air pump, and analyzed using methods such as gas chromatography/mass spectrometry (GC/MS), gas chromatography/flame ionization detection (GC/FID), or high performance liquid chromatography (HPLC). This provides qualitative and quantitative information on each VOC in the collected air sample. Integration analysis is recommended by some organizations for official VOC measurements [4,5]. However, air samples have to be taken over at least half an hour and up to a few hours. Therefore, only time-averaged information can be obtained. Furthermore, GC/MS, GC/FID, and HPLC analysis are relatively time consuming and complex compared to other techniques. This means that with integration analysis results cannot be obtained immediately.

Recently, several real time monitors for VOCs have been developed, and these utilize real time detectors such as a photo-ionization detector (PID) or semiconductor sensor. These monitors can determine the total VOC (TVOC) concentration within approximately several seconds. Furthermore, proton transfer reaction-mass spectrometry (PTR/MS) has drawn great deal of attention for the purpose. These techniques allow immediate and continuous monitoring of the variation in TVOC concentration with time. However, they cannot be used to determine the contribution of each individual VOC to the TVOC concentration.

The combination analysis with deferent techniques has been generally applied, such as combination use of GC/MS and PTR/MS. In this study, a more automatic combined system of integration analysis and real time monitoring (Peak Capture System; PCS) was developed. In this system, real time monitoring was used to predict future elevation in TVOC concentration (peak). This was used as an indicator of when to collect (capture) air samples for integration analysis. This enabled qualitative and quantitative analysis of individual VOCs when the TVOC concentration was high. For this system, we

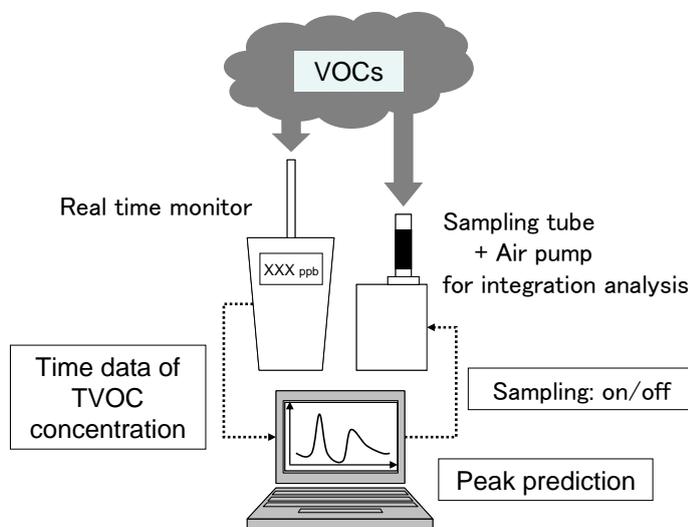
first developed an algorithm to predict the appearance of a peak in TVOC concentration, and then set up an automatic system to initiate air sampling for integration analysis. The PCS is particularly useful in cases where air pollution occurs intermittently and/or from unknown emission sources. It should be noted that the PCS can also be applied to on-demand measurements. Studies of VOCs emissions from plants and vegetation would be suitable application of such a combination measurement [6]. In this study, we applied the system to auto-sampling and analysis of VOCs in a conventional house. This system will be particularly effective in cases of intermittent air pollution from unknown emission sources.

**2. Experimental Section**

*2.1. Physical Setup of the PCS*

The PCS is illustrated in Figures 1 and 2. The system included a computer that could forecast TVOC concentration elevation from a prediction algorithm.

**Figure 1.** The Peak Capture System.



**Figure 2.** Photograph of the Peak Capture System.



Connected to the computer were a real time monitor (PID monitor, ppb RAE plus, RAE systems, USA), and an air sampling pump and sorbent tube for integration analysis. The real time monitor continuously monitored the TVOC concentration in ambient air. Chemical compounds in vacuumed air were ionized by ultraviolet light (10.6 eV) in the monitor [7]. The ionized molecules were collected to the electrode and the current was measured. The TVOC concentration was estimated from the current. The detection range of the PID monitor was 0–9,999 ppb, which provided a resolution of 1 ppb. The TVOC concentration data were output continuously as analog voltage variation and converted to digital data in a converter (NI USB-6009, National Instruments, US). The converted dataset was sent to the computer, and the TVOC concentration elevation profile was forecasted using the prediction algorithm written with Microsoft Visual Basic 6.0 (see Figure 3 in the next section for data processing flowchart). This was used to determine the start point for air sampling by the pump/sorbent tube for integration analysis. The computer automatically stopped the sampling pump after the sample had been taken. The sorbent tube was replaced manually after each sample was taken. The system is small enough to be transported in the field.

## 2.2. Peak Prediction Algorithm

An algorithm to forecast the TVOC concentration elevation profile from the dataset of historical variation in TVOC concentration was required. This also needed to be optimized for the specific objectives of the study. For this purpose, we adopted a method using two moving averages to predict the future elevation of TVOC concentration.

Moving averages are generally used with time series data to smooth out short-term fluctuations and highlight longer-term trends. The simple moving average (SMA) at time  $t$  is obtained as the mean of  $n$  previous data points:

$$SMA = \frac{(p_t + p_{t-1} + p_{t-2} + \dots + p_{t-n+1})}{n} \quad (1)$$

where  $p_t$  is the value of the datum at time  $t$ . With larger  $n$ , SMA provides better smoothing of short-term fluctuations, and particularly highlights longer-term trends but not short-term trends.

To predict the future trends in variation of TVOC concentration with time we utilized both the long-term moving average (LTMA) and short-term moving average (STMA). When the STMA crosses above the LTMA, this is a signal that the data is increasing in value. This method is often used in technical analysis of stock market or other financial data, where the crossover of the two moving averages is termed the golden cross. In technical analysis the golden cross is considered to signal a rise in stock price. The time periods for each moving average, which dictate the number of data points averaged, are first and second parameters in the algorithm. These should be optimized according to the measurement objectives of the study.

As a third parameter, we introduced a threshold value for determination of a peak. In cases where the difference between the STMA and the LTMA exceeds this threshold value, a peak is predicted and the algorithm signals for an air pump to start air sampling (Figure 3). In contrast, when this difference is below the threshold, a sampling signal is not produced and the system continues monitoring the concentrations. This avoids erroneous peak predictions from small fluctuations in the concentration of the TVOC.

**Figure 3.** Flowchart for the TVOC concentration elevation prediction algorithm.

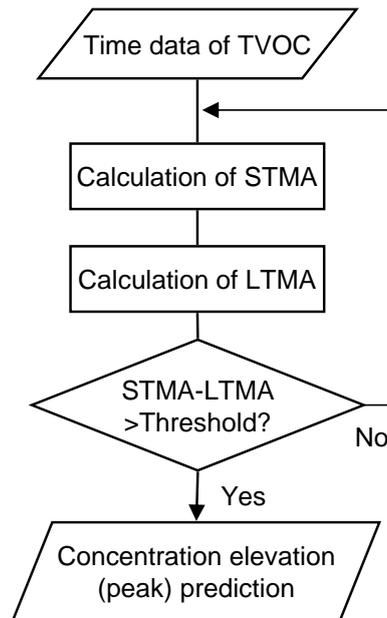
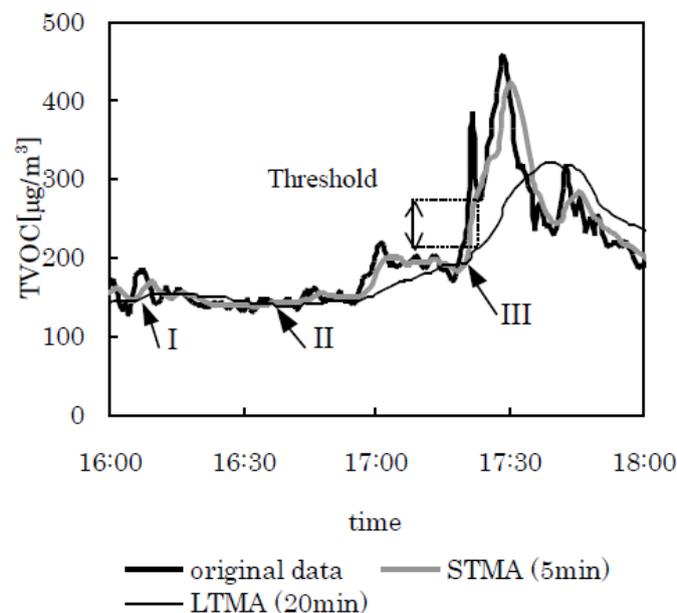


Figure 4 illustrates the actual data from measuring the variation of TVOC concentration with time in a conventional house with the PID. The moving averages for these data are also illustrated.

**Figure 4.** Example of the variation in TVOC concentration in a conventional house, and the moving averages. Three golden crosses, points I–III are apparent. However, cross points I and II are only small fluctuations, and the concentration did not increase after these points.



The TVOC concentration was measured at 1 min intervals. The data points were averaged over 5 min and 20 min for STMA and LTMA, respectively. Without the third parameter, three golden crosses were apparent. This was due to erroneous detection of small fluctuations, such as those at

points I or II, as predictors of an increase in concentration. These results illustrate that the third parameter should also be included, and its level determined depending on the objectives of the measurement.

The practical focus of our study was to measure the concentrations of VOCs in indoor air of conventional houses in Japan. Hence, we optimized the three parameters in the algorithm using 22 data sets of TVOC concentrations measured over 24 h in conventional Japanese houses. We then evaluated whether the algorithm could correctly predict increases in the TVOC concentration.

### 2.3. Integration Analysis

Thermal desorption tubes (Stainless steel, ID: 5 mm × 90 mm) filled with two sorbents, 100 mg of Tenax TA (Supelco Inc., USA) followed by 70 mg of Carboxen-1000 60/80 (Supelco Inc., USA), were used to collect VOCs. A portable pump (MP-Σ 30, Sibata Scientific Technology Ltd., Japan) set to a flow rate of 100 mL/min was used for air sampling. This pump was modified so that computer can control its start and stop. The samples were analyzed via an automatic thermal desorber (ATD650 TurboMatrix, Perkin Elmer Inc., USA) directly connected to a GC (HP6890, Hewlett Packard Co., USA) with MS (HP5973, Hewlett Packard Co., USA). Carbonyl compounds were collected in 2,4-dinitrophenyl-hydrazine (DNPH) cartridges (XpoSure Aldehyde Sampler, Waters Ltd., USA) with the modified pump at 1 L/min. The carbonyl DNPH derivatives were extracted from the cartridge with 10 mL of acetonitrile (HPLC grade, Wako Pure Chemicals Co. Ltd., Japan). The carbonyl-DNPH derivatives were analyzed with a HPLC (HP1100, Hewlett Packard Co., USA) with a photo diode array detector. All other analytical conditions are summarized in Table 1.

**Table 1.** Analytical conditions for ATD/GC/MS and HPLC.

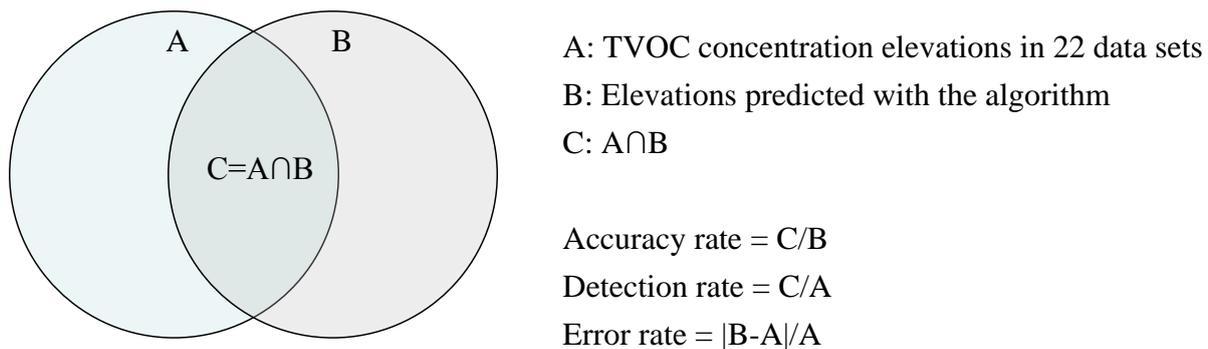
ATD/GC/MS		
ATD	First desorption	300 °C (10 min)
	Second desorption	5 °C → 40 °C/min → 300 °C (10 min)
GC	Column	HP-1 MS (60.0 m × 250 μm, 1.00 μm)
	Carrier gas	He
	Column temperature	40 °C (4 min) → 7 °C/min → 280 °C (10 min)
MS	Analytical mode	SCAN
	Mass range	m/z = 33–550
HPLC		
	Column	Ascentis RP-Amide (250 mm × 4.6 mm, 5 μm)
	Mobile phase	H <sub>2</sub> O : CH <sub>3</sub> CN = 35 : 65
	Flow rate	1.0 mL/min
	Injection volume	20 μL
	Column temperature	35 °C
	Detector	Diode Array Detector 360 nm

### 3. Results and Discussion

#### 3.1. Optimization of the Elevation Prediction Algorithm

The three parameters in the elevation prediction algorithm were optimized using 22 data sets of TVOC concentrations measured over 24 h in conventional Japanese houses. The total number of elevations in these data was counted at 83 by experts in the field of air pollution measurement. To optimize the three parameters in the algorithm, we used three indicators: the accuracy rate, the detection rate, and the error rate (Figure 5).

**Figure 5.** Optimization indicators for the elevation prediction algorithm.



If the algorithm is perfectly optimized, the accuracy rate, detection rate, and error rate will be equal to 1, 1, and 0, respectively. Setting of the parameters also strongly depends on the measurement situation and objectives. We varied the time period for the LTMA from 10 to 60 min with a fixed time period for the STMA (5 min) and fixed threshold (20 ppb). The time period for the STMA was set low (5 min) to allow rapid elevation predictions. The threshold value was determined based on the error range of the PID (20 ppb).

**Figure 6.** Performance of the algorithm, illustrating changes in the optimization indicators with variation of the LTMA time period.

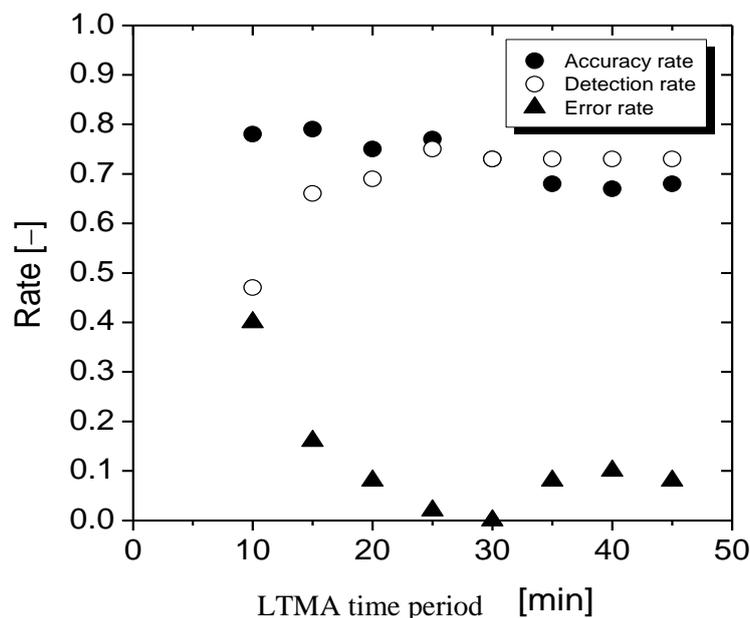


Figure 6 shows the performance of the algorithm under these conditions. With an increase in the time period for the LTMA, the accuracy of the algorithm slightly decreased, the detection rate rapidly increased, and the error rate decreased. Both the accuracy rate and detection rate leveled off above a LTMA time period of 20 min. Hence, we set the three parameters as follows: STMA = 5 min, LTMA = 20 min, threshold = 20 ppb. Using these conditions, 76 of 83 elevations could be forecast before their appearance. These values were used for the algorithm parameters in subsequent experiments. In addition to measuring TVOC concentrations at predicted peaks, the background concentration was also measured when the TVOC concentration was low. The timing for background concentration measurements was determined from the absolute value of the TVOC concentration.

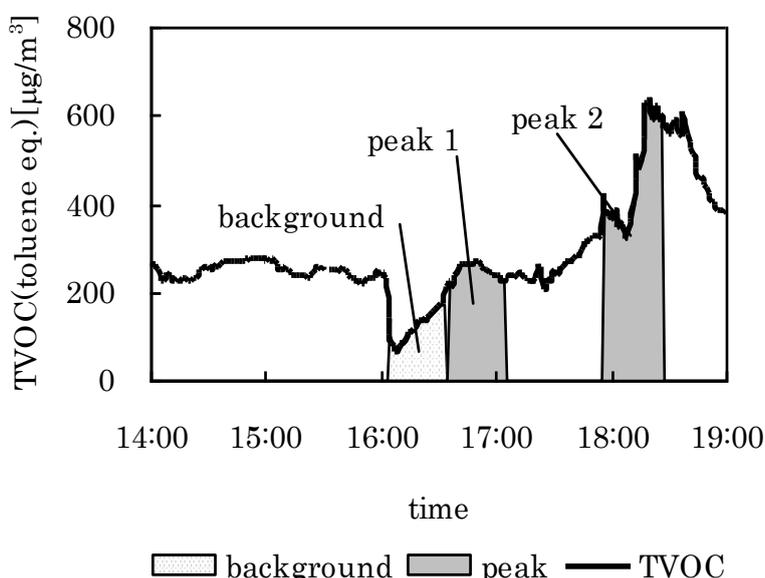
### 3.2. Application of the PCS with Optimized Algorithm to Indoor Air Measurements

The developed PCS with the optimized algorithm was then applied to indoor air TVOC measurements in conventional houses in Japan.

#### Case 1

Measurements for Case 1 were conducted in one house over 24 h in January in 2008. Air samples were automatically collected with the PCS using the optimized algorithm parameters. Sampling times were set to occur 30 min after a prediction of increasing concentration. Background TVOC samples were automatically collected when the TVOC concentration was lower than 100 ppb. Four elevations appeared over the time period of the experiment. Figure 7 shows a typical section of the results. Integration analyses for the background and peak times were used to determine the chemical compounds that had higher concentrations during peak times than in the background period (Table 2).  $\alpha$ -pinene and *p*-dichlorobenzene are commonly used as room deodorants or insect repellents. It is assumed that the observed TVOC variation was caused by use of these items.

**Figure 7.** Variation of TVOC concentration with time, and periods predicted and sampled as peak concentrations in Case 1.

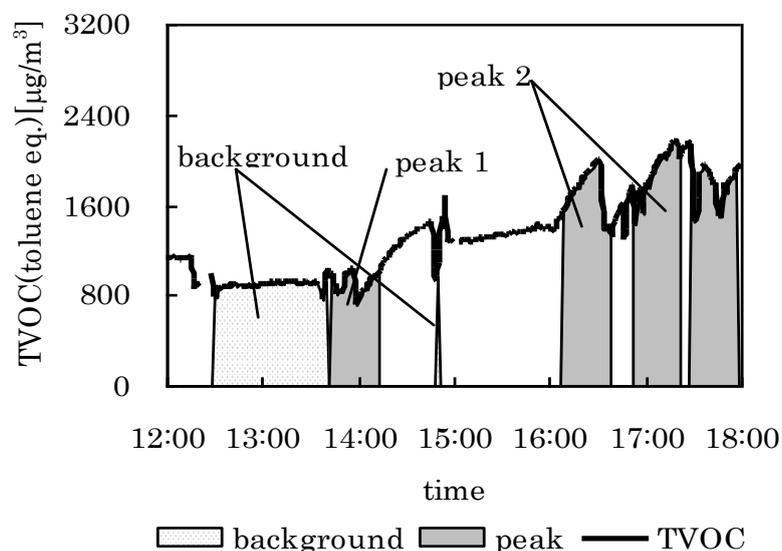


**Table 2.** Result of integration analysis in Case 1 ( $\mu\text{g}/\text{m}^3$ ).

	Background	Peak 1	Peak 2
Acetaldehyde	<3	10	54
Acetone	6	46	75
<i>p</i> -Dichlorobenzene	<2	52	99
Nonanal	<17	43	70
$\alpha$ -Pinene	0.8	74	192
Styrene	<3	9	53
Undecane	<2	41	64
Others	12	256	241

## Case 2

Another measurement was also conducted in other house in January 2008. The values of the parameters and sampling times were same as in Case 1. In this case, the background samples were automatically collected when the TVOC concentration was lower than 400 ppb. The TVOC concentration was relatively higher than that observed in Case 1. This was due to use of an oil stove in this house. The results are shown in Figure 8 and Table 3. Over the 24 h measurement period, 14 peak samples were collected. A total of sixteen elevations occurred, but some were collected in the same sample tube. Chemical compounds that had higher concentrations during peak times than in the background period were detected using integration analysis (Table 3). During time of peak 2, hydrocarbons with relatively high molecular weight, e.g., decane, dodecane and undecane, were observed. It was assumed that these compounds originated from the fuel of oil stove. The concentration of butyraldehyde increased during peak times. This compound is usually contained in fruit perfumes or as ingredient in other fragranced products.

**Figure 8.** Variation of TVOC with time, and periods predicted and sampled as peak concentrations in Case 2.

**Table 3.** Result of integration analysis in Case 2 ( $\mu\text{g}/\text{m}^3$ ).

	Background	Peak 1	Peak 2
Butyraldehyde	209	643	251
Decane	13	13	55
Dodecane	7	6	50
Formaldehyde	7	36	116
Nonanal	<17	<17	81
Undecane	12	10	76
Others	115	19	535

#### 4. Conclusions

With its optimized algorithm the developed combined integration analysis and real time monitoring system, PCS, could predict the appearance of peaks in TVOC concentrations, and automatically collect selected ambient air samples. The analysis of air samples collected during peak times contributed to the identification of dominant pollutants. The results enabled an evaluation of possible VOC emission sources.

In future work, the elevation prediction algorithm and physical set up of the system need to be improved. An automatic system for changing air sampling tubes would contribute to more effective measurement. The PCS is particularly useful in cases where air pollution occurs intermittently, and from unknown emission sources. The system could effectively contribute to investigations of air pollution caused by a factory operations or the behavior of residents in a house. It should be noted that the PCS can also be applied to on-demand measurements, and application of the system to other measurements is expected. These could include average concentration measurement, which should avoid temporal high concentration periods. A further possible application is bottom concentration measurement, which would avoid over-collection of samples such as in sampling of asbestos fiber to facilitate accurate counting of fiber numbers.

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#### References and Notes

1. Andersson, K.; Bakke, J.V.; Bjørseth, O.; Bornehag, C.-G.; Clausen, G.; Hongslo, J.K.; Kjellman, M.; Kjærgaard, S.; Levy, F.; Møhlave, L.; Skerfving, S.; Sundell, J. TVOC and health in non-industrial indoor environments: Report from a nordic scientific consensus meeting at Långholmen in Stockholm. *Indoor Air* **1997**, *7*, 78-91.
2. Cullen, M.R. The worker with multiple chemical sensitivities: An overview. *Occup Med.* **1987**, *2*, 655-661.
3. Møhlave, L.; Clausen, G.; Berglund, B.; Ceaurriz, J.; Kettrup, A.; Lindvall, T.; Maroni, M.; Pickering, A.C.; Risse, U.; Rothweiler, H.; Seifert, B.; Younes, M. Total Volatile Organic Compounds (TVOC) in indoor air quality investigations. *Indoor Air* **1997**, *7*, 225-240.

4. Health, Labour and Welfare Ministry of Japan. *Interim report of Investigative Commission on Sick House (Indoor Air Pollution), Summary of the 1st to 3rd Meeting, Sampling Methods for Chemical Pollutants in Indoor Air and Its Measurement Methods* (in Japanese), 2000; Available online: [http://www1.mhlw.go.jp/houdou/1206/h0629-2\\_b\\_13.html](http://www1.mhlw.go.jp/houdou/1206/h0629-2_b_13.html) (accessed on 25 November 2010).
5. ECA-IAQ (European Collaborative Action). *Indoor Air Quality and Its Impact on Man*; Report No.19; Luxembourg office for official publications of the European Community: Luxembourg, Germany, 1997.
6. Tholl, D.; Boland, W.; Hansel, A.; Loreto, F.; Röse, U.S.R.; Schnitzler, J.-P. Practical approaches to plant volatile analysis. *Plant J.* **2006**, *45*, 540-560.
7. RAE Systems. *Application and Technical Notes*, 3rd ed.; RAE Systems World Headquarters: San Jose, CA, USA, 2005.

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