Green analytical methodologies for environmental chemical pollutants: Evaluation of various measurement methods of formaldehyde in indoor air by Environmental Efficiency

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1. Introduction

Green analytical chemistry, firstry stated by Namiesnik in 1999, is a concept based on the Green chemistry[1]. Goal of green analytical chemistry is to use analytical procedures that generate less hazardous waste and that are safer to use and more benign to the environment (Keith *et al*.,2007). Since 1999, the number of papers related to the green analytical chemistry has been increasing every year[2] (Fig.1). However, it is difficult to identify the greenness and evaluate what extent the procedure becomes green. Then, authors have developed a novel evaluation method of the greenness on the analysis of environmental chemical pollutants.

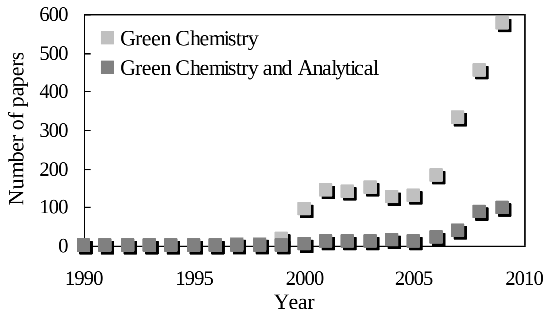

Fig.1 Number of papers resulting from J-Dream II for 1990-2009 for keywords "green chemistry" (■) and "green chemistry and analytical"(▲). J-Dream II is operated by Japan Science and Technology Agency.

2. Definition of AEE

In our evaluation, the greenness is expressed as Analytical Environmental Efficiency (AEE). AEE is given by ratio between its analytical performance such as sensitivity and repeatability and environmental load including dosage of reagent, energy consumption, and disposal instruments (E-1). It is possible to quantify the degree of greenness of analytical methods for environmental pollutant substances.

$$\text{AEE} = \frac{[\text{Analytical performance}]}{[\text{Environmental load}]} \quad \cdots \textbf{E-1}$$

The higher the value of AEE, the degree of greenness is higher. The analytical performance consists of two elements, while the environmental load consists of three elements. These elements are calculated from following equations.

【Analytical performance】

Analytical performance is expressed as a product of sensitivity and repeatability. These parameters were calculated according to the following equations. The calculated values were then converted to a score from 1 to 5. The high score shows goodness of analytical performance.

①Sensitivity, *S*

$$S = \frac{[\text{Limit of quantification}]}{[\text{Environmental standard}]}$$

[Score] $S > 0.2 \rightarrow 1$, 0.2~0.1→2, 0.1~0.05→3
0.05~0.033→4, $S < 0.033 \rightarrow 5$

②Repeatability, *R*

$$R = [\text{CV of repeated measurements}]$$

[Score] $R > 20\% \rightarrow 1$, 20~15%→2,
15~10%→3, 10~5%→4, $R < 5\% \rightarrow 5$

【Environmental load】

Environmental load is expressed as a product of dosages of reagents, energy consumption, and amount of disposal instruments, normalized to the amount of analytes.

③Dosages of reagent, *D*

$$D = \frac{[\text{Total dosages of used reagents}]}{[\text{Amount of analytes}]}$$

$$\left(\begin{array}{l}\text{Amount of}\\ \text{analytes}\end{array}\right) = \left(\begin{array}{l}\text{Environmental}\\ \text{standard}\end{array}\right) \times \left(\begin{array}{l}\text{Sampling amount of}\\ \text{environmental media}\end{array}\right)$$

[Score] $D > 10{,}000 \rightarrow 5$, 10,000~1,000→4,
1,000~100→3, 100~10→2, $D < 10 \rightarrow 1$

The undesired property for environment was also considered for scoring the reagent. Greenness profile Symbol, proposed by Keith *et al*., was used as a weighting factor for considering undesired property of a reagent (Fig.2). When the reagent has some of the properties, the score of *D* was then multiplied by the number of item plus one.

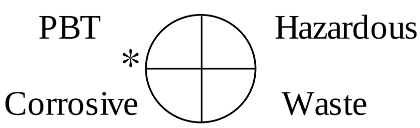

Fig.2 The greenness profile symbol[3]. (＊persistent,bioaccumulate,toxic)

④Energy consumption, E

Energy consumption during the course of analysis was converted into the amount of CO_2 emissions.

$$E = \frac{[\text{Amount of } CO_2 \text{ emissions}]}{[\text{Amount of analytes}]}$$

[Score] E >10,000,000→5,
10,000,000~10,000→4, 1,000~100→3,
100~10→2, E <10→1

⑤Disposal instrument, I

Use of reusable instruments is favorable for the green process. Then, amount of disposal instruments such as DNPH cartridge and Gas detector tube are accounted for the environmental load.

$$I = \frac{[\text{Weight of disposal instruments}]}{[\text{Amount of analytes}]}$$

[Score] I >500,000→5, 500,000~1,000→4,
1,000~100→3, 100~10→2, I <10→1

3. AEE evaluation

3-1 Importance of formaldehyde measurement

Formaldehyde has been regarded as a most important indoor air pollutant with largest number of papers presented at the annual meeting of Society of Indoor Environment, Japan from 1998 to 2010 (Fig.3). Then, the greenness of the analytical methods of formaldehyde was evaluated by AEE and a novel green method was proposed in this study.

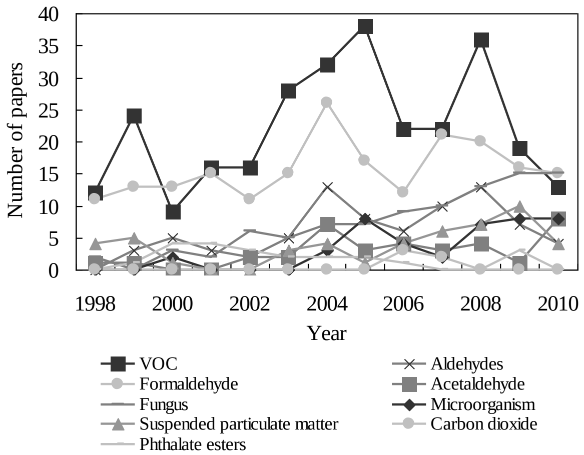

Fig.3 Chemicals appeared in the papers submitted to annual meetings of SIEJ.

3-2 Comparison of the AEE

As a case study, authors have evaluated two kinds of analytical methods of formaldehyde in indoor air; a previous standard method using a DNPH active sampling coupled with HPLC analysis, and an alternative method using a fast passive sampler[4] and HPLC with a semi-micro column (Fig.4).

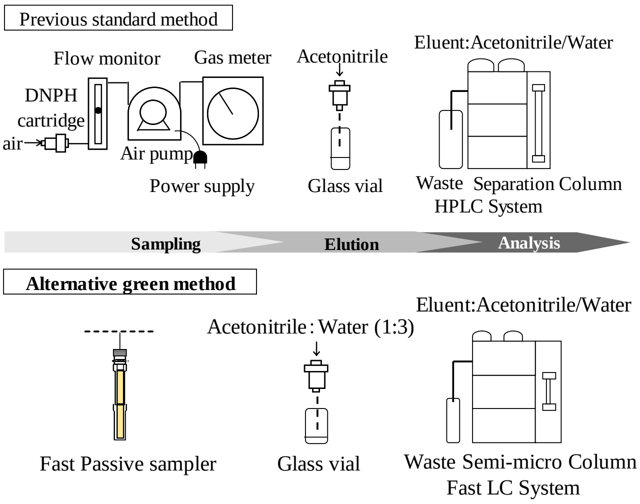

Fig.4 Proposal of alternative green methodology for the measurement of formaldehyde in indoor air.

The terms related to their performance and environmental loads were listed up and then scored by their degrees (Table1). Comparison of the calculated AEEs of both methods showed the alternative passive sampler method was about two times greener than the previous standard method (Fig.5), mainly reducing the power supply in sampling and amount of eluent (acetonitrile) in the HPLC analysis.

Table 1 Comparison of the calculated AEEs.

	Previous standard method		Alternative green method	
	Calculated Value	Score	Calculated Value	Score
①Sensitivity	0.0077	5	0.0228	5
②Repeatability	4.4%	5	4.5%	5
③Dosages of reagent	6,500,000	10	6,500	8
④Energy consumption	24,000,000	5	910,000	4
⑤Disposal insturument	1,160,000	5	5268	3
AEE	0.1		0.26	

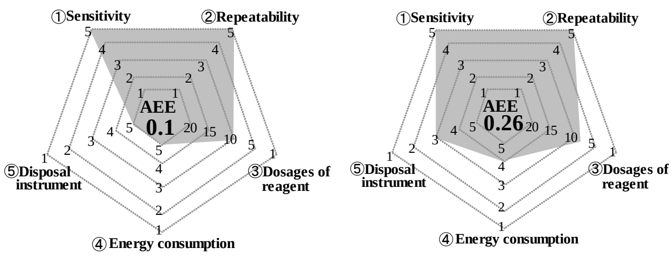

Fig.5 Comparison of the calculated AEEs.
(Left: Previous Standard method, Right: Alternative green method)

4. Conclusion

This study demonstrated the possible application of AEE for the evaluation of greenness profiles of analytical methods.

5. Reference

1)J. Namiesnik, *Environ. Sci. Pollut. Res*. 6, 243 (1999)
2)A. Kawamura, *et al., Sym. Environ. Chem. Pro. Abst.*, 9 (2010)
3)L. K. Keith, *et al*., *Chem. Reviews*, 107, 2695-2708 (2007)
4)Y. Sekine, *et al*., *Appl. Surf. Sci*., 238, 14-17 (2004)