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授与した学位	博 士
専攻分野の名称	学 術
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学位授与の要件	自然科学研究科機能分子化学専攻 (学位規則第5条第1項該当)
学位論文の題目	Studies on Development of Novel Detection Reactions for Formaldehyde and Ammonia and Their Application to Analytical Chemistry (ホルムアルデヒド及びアンモニアの新規検出反応の開発と分析化学への応用に関する研究)
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### 学位論文内容の要旨

This work describes the development of novel detection reagents for formaldehyde and ammonia determination based on the modified Hantzsch derivatization. Several kinds of commercially available  $\beta$ -diketone analogues and  $\beta$ -keto esters were examined by using spectrophotometric and fluorometric methods. Applications of these developed methods are carried out to the environmental samples by batchwise and flow-based analysis methods.

The new method with a novel reagent, acetoacetanilide, for the determination of formaldehyde was established; it is based on the reaction of formaldehyde with acetoacetanilide and ammonium acetate. The reaction could be carried out at room temperature without any heating system. The reaction conditions were optimized by a batchwise procedure, and the product was detected by spectrophotometry and fluorometry. The flow injection analysis (FIA) was employed for the application of the new fluorometric detection for the determination of formaldehyde in order to obtain higher sensitivity. The proposed method shows a good linearity from 0.50 to  $40 \times 10^{-7}$  M, and the limit of detection (LOD) of  $3 \times 10^{-9}$  M (0.09 ppb) is achievable. The method can be directly applied to the determination of formaldehyde in the environmental water samples at low concentration levels without any enrichment procedure. A novel water-soluble reagent, methyl acetoacetate, was for the first time proposed for the specific spectrophotometric determination of formaldehyde. The method is based on the reaction of formaldehyde with methyl acetoacetate in the presence of ammonia. An inexpensive light emitting diode (LED)-based UV detector (375 nm) was, for the first time, used. Under the optimized experimental conditions, formaldehyde in an aqueous solution was determined over the concentration range from 0.25 -  $20.0 \times 10^{-6}$  M with a linear calibration graph. The relative standard deviation of 12 replicate measurements of  $5 \times 10^{-6}$  M formaldehyde was 1.2 %. The proposed method was successfully applied to the determination of formaldehyde in natural water samples.

The extension of the Hantzsch reaction to the assay of ammonia was proposed. Hantzsch reaction was modified by using acetylacetone as a detection reagent and was for the first time applied to the determination of ammonia. The yellow color product, 3,5-diacetyl-1,4-dihydrolutidine, was detected fluorometrically at an excitation wavelength ( $\lambda_{ex}$ ) of 420 nm and an emission wavelength ( $\lambda_{em}$ ) of 505 nm. The method was successfully applied to ammonia determination in the atmosphere using flow injection fluorometric method. Then, the following novel detection reagents were proposed: methyl acetoacetate, ethyl acetoacetate, n-propyl acetoacetate, n-amyl acetoacetate and acetoacetanilide were examined by using spectrophotometric and fluorometric methods. Of these reagents, methyl acetoacetate gave the largest molar absorptivity ( $5.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 60 °C) and is one of the most soluble reagents in water. Moreover, methyl acetoacetate is the most reactive with ammonia, selective and sensitive for ammonia. Therefore, a new and specific detection method for the spectrofluorometric determination of ammonia was developed. A flow injection method is applied for the determination of ammonia in environmental water and the detection limit of  $8 \times 10^{-8}$  M (S/N=3) were obtained.

## 論文審査結果の要旨

This work focuses on the development of novel detection reagents for formaldehyde and ammonia determination based on the Hantzsch derivatization. Several kinds of commercially available  $\beta$ -diketone analogues and  $\beta$ -keto esters were examined by using spectrophotometric and fluorometric methods. Applications of these developed analytical methods are carried out for environmental samples by using a batchwise and a flow-based analysis method.

The new method with a novel reagent, acetoacetanilide, for the determination of formaldehyde was established. The reaction could be carried out at room temperature without any heating system. The flow injection analysis (FIA) was employed for the application of the new fluorometric detection for the determination of formaldehyde in order to obtain higher sensitivity. The proposed method shows a good linearity from 0.50 to  $40 \times 10^{-7}$  M, and the limit of detection (LOD) of  $3 \times 10^{-9}$  M (0.09 ppb) is achievable. A novel water-soluble reagent, methyl acetoacetate, was, for the first time, proposed for the specific spectrophotometric determination of formaldehyde. The method is based on the reaction of formaldehyde with methyl acetoacetate in the presence of ammonia. An inexpensive light emitting diode (LED)-based UV detector (375 nm) was, for the first time, used. The relative standard deviation of 12 replicate measurements of  $5 \times 10^{-6}$  M formaldehyde was 1.2 %. The proposed method was successfully applied to the determination of formaldehyde in natural water samples.

Also, the extension of the Hantzsch reaction to the assay of ammonia was proposed. Hantzsch reaction was modified by using acetylacetone as a detection reagent and was, for the first time, applied to the determination of ammonia. The method was successfully applied to ammonia determination in the atmosphere using flow injection fluorometric method. The detection reaction is very specific and sensitive for ammonia. The standard deviation (RSD) of 2.1 % ( $n = 7$ ) for  $5 \times 10^{-6}$  M ammonium chloride solution and the detection limit of  $8 \times 10^{-8}$  M ( $S/N=3$ ) were obtained. A flow injection method is applied for the determination of ammonia in environmental water samples.

In conclusion, the thesis submitted is worthy to be admitted as a doctoral thesis (Ph.D.).