NITROGEN TRICHLORIDE (NCl_3) DETERMINATION IN INDOOR SWIMMING POOLS: PROPOSAL FOR A NEW METHOD.

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ABSTRACT

The aim of this study was to identify a new analytical method for NCl_3 air determination that could be used directly in swimming pool facilities for the human exposure assessment procedures. This new protocol is based on a colorimetric reaction commonly employed to detect the total and free chlorine levels in water. Particularly, it allows the entrapment of NCl_3 in ambient air into a water solution containing diethyl-p-phenylenediamine and potassium iodide. NCl_3 from the air environment reacts with potassium iodide realising iodine, which reacts with diethyl-p-phenylenediamine and produces a pink colour. The intensity of the colour is proportional to the amount of NCl_3 from the sampled indoor swimming pool air, and can be easily measured using a portable photometer for DPD analyses. The proposed method has been validated in terms of linearity, limit of detection (LOD) and repeatability. We tested the linearity by creating an artificial swimming pool environments under a closed chemical safety cabinet, and reading solutions of NCl_3 in air sampling deriving from standards in water at different concentrations (5, 10, 20 mg/L of NCl_3 standards). The actual concentration of NCl_3 in the water was verified by adopting the same DPD method used in the real swimming pools. This linearity test was repeated three times and showed R^2 values of: 0.996; 0.998 and 0.996. The LOD measured as standard deviation was 3.6 $\mu g/m^3$, while the LOD measured according to the instrument sensitivity was 8.5 $\mu g/m^3$. The repeatability showed a coefficient of variation (CV%) equal to 1.7%. In conclusion, this method is easy to use, efficient and economical and does not use toxic substances.

Keywords | Nitrogen trichloride, ambient air, indoor swimming pools, new method.

INTRODUCTION

It is well known that water disinfection treatments in indoor swimming pools generate a mixture of potentially harmful disinfection by-products (DBPs) (WHO, 2006). Among them, nitrogen trichloride (NCl_3), a powerful irritant, has been linked with respiratory symptoms and asthma in swimmers, mainly in children, and in occupationally exposed subjects (Jacobs et al., 2007, Weisel et al., 2009). Accurate NCl_3 exposure assessment in indoor swimming pools is difficult, because NCl_3 presence in air is influenced by different factors, including the pool water quality and the number of swimmers in the pool. Moreover, the analytical method usually adopted for the determination of NCl_3 in air samples shows some problems such as the use of particular filters for the air sampling procedures and the expensive instrumental equipments for the laboratory quantification of this volatile DBPs (Hery et al., 1995).

The aim of this study was to develop a simple method for NCl_3 air determination that could be used directly in swimming pool facilities for the human exposure assessment procedures.

The proposed method is based on the entrapment of NCl_3 in air (trough an air pump and impingers) in a water solution where diethyl-p-phenylenediamine and potassium iodide, the reagents commonly

used to detect total and free chlorine levels in water according to the Palin method, were previously added (Palin, 1957). The entrapment is performed by an active sampling procedure using an air pump connected to two impingers. NCl_3 in water solution reacts with potassium iodide realising iodine, which reacts with diethyl-p-phenylenediamine and produces a pink colour. The intensity of the colour is proportional to the amount of NCl_3 from the sampled indoor swimming pool air, and can be easily measured using a portable photometer.

EXPERIMENTS

Device and apparatus. Environmental air samples were collected by a simple apparatus consisting of two glass impingers (Impinger 1 and Impinger 2), with a minimum reservoir of 40 ml and fritted glass stem with a porous septum (101 – 160 µm) (INCOFAR - ITALY), a 250 ml flask with stopcocks, used as security tank and, finally, an air sampling pump (PUMP™ Buck P.N. APB-921000, range 5-5000 mL/min - SUPELCO - USA). The quantitative analyses of free and total chlorine in water were performed by a portable photometer (PC Compact – Aqualytic).

Standards and reagents. For the determination of chlorine in water, diethyl-p-phenylenediamine (DPD 1) and potassium Iodide (DPD 3) commercial tablets (Aqualytic) were adopted.

Given the lack of commercial NCl_3 standard solutions, we prepared our standards according to the protocol suggested by Shang and Blatchley III, (1999). The solutions were prepared from reagent-grade chemicals and diluted to target concentration using reagent grade water.

Stock chlorine solution was prepared from 5% sodium hypochlorite (NaOCl), diluted to 4000–5000 mg/L as chlorine, and stored in aluminium foil-covered glass-stoppered flasks. Chlorine standard solutions were prepared by dilution with phosphate buffer (pH 7). NCl_3 standard solutions were prepared daily by mixing a free chlorine solution with an ammonium chloride (NH_4Cl) solution at a chlorine to ammonia molar ratio of 3.15: 1.00 and standardised titrimetrically. Both solutions were adjusted to pH 5 with acetic acid (1 M) prior to mixing.

Sample collection. An active air sampling with a constant flow air sampling pump at a flow rate of 1000 ml/min for 100 minutes was performed to sample around 100 litres of swimming pool air, normalized by 25 °C and 1013 hPa. In order to avoid contamination from free and combined chlorine in the water aerosol, the sampling apparatus was located at 1.5 m from the floor surface and not less than 2 m from the pool edge. Both impingers were filled with 15 ml of reagent grade water and a DPD1 and DPD3 tablet (Aqualytic): the tablets were dissolved using a glass rod.

Determination of NCl_3. To quantify the amount of NCl_3 in the indoor swimming pool air, the solutions derived from the two impingers were transferred into two 25mL graduated flasks, washing the inside and the porous septums of the impingers. The obtained target volumes were mixed and immediately analysed by using a photometer (PC Compact – Aqualytic). The solution from Impinger 2 was considered as reagent blank as it verifies if NCl_3 has completely saturated Impinger 1. The final value was the difference between the two analytical readings. In order to convert the obtained residual chlorine concentration (expressed in mg/L Cl) in micrograms per cube meter of NCl_3, we applied a simple stoichiometric conversion.

RESULTS

The proposed method has been validated in terms of linearity, limit of detection (LOD) and repeatability. The linearity was tested in our laboratory by creating an artificial swimming pool environment under a closed chemical safety cabinet, and reading solutions of NCl_3 in air sampling deriving from standards in water at different concentrations (5, 10, 20 mg/L of NCl_3 standards). The actual concentration of NCl_3 in the water was verified by adopting the same DPD method used in the real swimming pools. The linearity test was repeated three times and showed R^2 values of: 0.996; 0.998 and 0.996.

The limit of detection (LOD) was determined according to two procedures. Both as 3-fold the standard deviation of the lowest NCl_3 standard solution (5 mg/L) used in the analytical runs from the linearity test, and considering the minimum instrumental reading: 0.01 mg/L per 100 litres of sampled air. The

LOD measured as standard deviation was 3.6 µg/m^3, while the LOD measured according to the instrument sensitivity was 8.5 µg/m^3.

The repeatability of the method was estimated by analyzing the same air sample of NCl_3 derived from a standard solution of 10 mg/L in the water of the simulated swimming pool, which was repeated 8 times. The CV% was then calculated. The repeatability showed a coefficient of variation (CV%) equal to 1.7%.

CONCLUSIONS

The proposed method, which is patent pending, is a method that does not use toxic substances, is easy to use, efficient and economical and gives good results in terms of linearity and repeatability. We believe that it is a suitable method to monitoring NCl_3 air levels from the chlorinated indoor swimming pool environment.

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