

Objective Evaluation Method for Chlorine Detector Tubes

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ABSTRACT

A tristimulus colourimetric method for the evaluation of detection response of chlorine detector tubes has been developed. The method is based on the suction of chlorine through the respective tube, followed by objective evaluation of the colouration change by means of a reflectance spectrophotometer. This eliminates errors in evaluation and allows identification of further positive attributes of detector tubes (e.g. response time, limit of detection). The method is suitable for tubes produced by various manufacturers. Oritest, Dräger and Gastec tubes were selected and measured. The response time of tubes lasted up to 30 s. The limit of detection was lowered up to four times. Reflectance curves of tubes before and after colouration change were recorded. The method also created the possibility of quantitative measurement by non-quantitative detector tubes.

Keywords: Detector tubes, reflectance, tristimulus colourimetry, detection effect

1. INTRODUCTION

In military practice, chlorine is well-known as the chemical warfare agent that initiated the beginning of modern chemical warfare due to its unprecedented effects¹. Nowadays it is an important component in the production of chemicals, plastic materials, polyurethane, polycarbonates, disinfectants or paper products²⁻⁷. There is a wide supply of chlorine in Europe and the amount is continually rising^{8,9}. Chemically, chlorine is a yellow-green gas with an irritant odour. Exposures must not exceed 1.5 mg/m³ for up to 6 h of work¹⁰.

Chlorine is a formidable agent because of military or terrorist organisations' interests¹¹ and other possible threats (e.g. industrial accidents¹²), it can be detected using many methods, e.g. spectroscopy¹³, separation¹⁴ or electrochemical¹⁵ analysis. In field conditions colourimetric detector tubes are widely used. There are plenty of producers of chlorine detector tubes. Frequently the reaction principle is based on oxidation of o-tolidine by chlorine, where a yellow orange reaction product is created¹⁶. Dräger (Germany)¹⁷ and Gastec (Japan)¹⁸ provide tubes that change their colouration, and according to the length-of-stain of the layer the manipulator is able to recognize the concentration of measured gas. Chlorine tubes are also produced by Kitagawa (Japan), MSA, and RAE Systems (both USA). The Czech producer Oritest provides the DT-003 detector tube. The reaction mechanism is based on the reaction of chlorine with potassium bromide, releasing bromine that creates a red product with fluoresceine¹⁹. Oritest tubes are cheap but not designated for quantitative measurements. Because of chemism types used in the tubes (o-tolidine or fluoresceine oxidation) all manufacturers declare interferences by other oxidizing chemicals (e.g. bromine, iodine, nitrogen oxides)¹⁷⁻¹⁹.

Evaluation of the detection effect of all presented tubes is performed visually on the basis of the operator's subjective perception. Although there are many drafts of devices for colouration registration²⁰⁻²⁷, the detection is evaluated merely visually, even at the quality control stage of the manufacturing process.

The aim of the study is to describe a method for objective evaluation of detection effect of detector tubes for chlorine suitable for tubes produced by various manufacturers. Using an objective evaluation method, important features of detector tubes can be verified or determined and a comparison of tubes can be performed. Declared features of studied detector tubes are displayed in Table 1. We assumed that by objectification, more preferable attributes of tubes could be reached.

Table 1. Declared characteristics of studied detector tubes- limit of detection (LOD), response time and calibration range¹⁷⁻¹⁹

Detector tube	Producer	LOD (mg/m ³)	Response time (s)	Calibration range (mg/m ³)
DT-003	Oritest	3	60	-
Chlor 0.2/a	Dräger	0.6	20	10-95
8H Chlorine	Gastec	16	45	79-3160

As an applicable method, tristimulus colourimetry based on the CIE-L*a*b* space was chosen. This is an analytical method used in the printing²⁸, textile²⁹ and automotive industries³⁰. Mainly, however, it has been used in connection to detector tubes^{31,32}. This method matches each colour with specific values by means of trichromatic system. Using this method it is possible to measure colour differences in CIE-L*a*b* colour space. This is a system of values that can be

transformed into basic rectangular coordinates X , Y and Z . The L^* value describes lightness (100 for white, 0 for black), a^* is the axis for redness-greenness ($+a^*$ for red, $-a^*$ for green) and b^* denotes the axis for yellowness-blueness ($+b^*$ for yellow, $-b^*$ for blue). For the total colour difference dE , the value is defined:

$$dE = \sqrt{dL^{*2} + da^{*2} + db^{*2}} \quad (1)$$

2. EXPERIMENTAL

2.1 Chemicals and Equipment

The following chemicals were used for chlorine preparation: potassium permanganate and hydrochloric acid 35 per cent p.a. (both Lachner). For spectrophotometric measurements of prepared chlorine, the following chemicals were used: potassium cyanide, calcium hypochlorite (both Lachema), barbituric acid, pyridine, methylorange (all Sigma-Aldrich), hydrochloric acid 35 per cent p.a. and sodium hydroxide p.a. (both Lachner).

For purity measurements and spectrophotometry standard laboratory glassware (Simax), a potentiometer with accessories (HANNA Instruments) and UV-VIS Helios α spectrometer (Unicam) were used. For detector tubes response measurements, the following equipment was used: DT-003 (batch 382, Oritest), Chlor 0.2/a (batch EC-1251, Dräger) and 8H Chlorine (batch 40618, Gastec) detector tubes, micropipettes (Brand), glass tubes (Oritest), desiccator with stopcock DN 300 (Duran Group), 617 dm³-in-volume test chamber (Lamon), XDS-10C pump (BOC Edwards) with attached flow meter, Ultra Scan PRO spectrophotometer (Hunter Lab) with attached special holder for tubes, Easy Match QC software (Hunter Lab) and Microsoft Excel 2010 (Microsoft).

2.2 Procedures

2.2.1 Preparation of Chlorine

Chlorine used for measurements in the following steps was prepared each time in a desiccator with stopcock DN 300 as the test chamber. The desiccator (18.5 dm³ vol) was placed in a fume cupboard. For the purpose of creation of analyte, reagents were placed into a Petri dish on the bottom of the desiccator. This solution was the result of the miniaturization of processes performed in 617 dm³-in-vol test chamber which was then used as a control chamber. Chlorine was created using

the reaction of potassium permanganate with hydrochloric acid. The temperature inside the desiccator chamber was 25°C and was measured by a digital thermometer. Reagents were left for spontaneous reaction for 30 mins. The reaction occurred according to the reaction below:



2.2.2 Determination of Concentration inside the Test Chamber

Before the suction process was performed, the real concentration of measured agent in the test chamber outlet had been determined using UV/VIS spectrophotometry. A gas washing bottle was connected to the test chamber outlet using a silicon hose (Fig. 1). Another hose spliced the bottle with the pump and flowmeter. Using the pump, the air inside the chamber was sucked out through the gas washing bottle for 1 min with flow rate 1dm³/min. In the bottle was a reagents solution for spectrophotometric König-Zincke determination of cyanogen halides³³. Chlorine acted as the oxidizing agent and cyanogen chloride was formed from potassium cyanide³⁴. As an additive spectrophotometric method 1 mmol/dm⁻³ methylorange in pH 3 buffer solution was used as indicator of chlorine presence.

2.2.3 Collection of Samples

Collection of samples was performed by pumping the gas from the chamber through the outlet and selected detector tube using a XDS-10C pump (Fig. 1). The suction speed was regulated by an attached flowmeter at a speed of 1dm³/min. The time periods of the suction processes through the tubes and manipulation were performed according to the manual for each tube.

2.2.4 Evaluation by the Devised Method

For the evaluation of colouration changes, the Ultra Scan PRO spectrophotometer was used. For specific measurements a custom-made tube holder was applied. The aperture size on the holder was rearranged to the size of the specific tube layer. The spectrophotometer cooperated with Easy Match QC software installed on a desktop PC.

All tubes used were marked on 4 sides with a pen and on each side the colouration of each layer was measured



Figure 1. Sampling followed by spectrophotometric determination of chlorine concentration in the desiccator (left) and collection of sample from the 617 dm³-in-vol chamber

before the suction process was performed. After termination of the suction process the tube was immediately fitted into the detector tube holder and the colouration change response was measured continuously. The colouration of the layer in the 4 marked positions was also measured and compared with the colouration measured before the suction process (standard). Formerly, we had studied the impact of ambient air mixture on the colouration change and no changes in CIE- $L^*a^*b^*$ values were recorded.

3. RESULTS AND DISCUSSION

3.1 Response Time and Colouration Stability

Technical possibilities allowed the earliest response time measurement of the tubes at about 20 s or 25 s after the suction process termination being performed. Already at this time measured layers had significantly changed their colouration. Recognizable changes of CIE- $L^*a^*b^*$ values were registered 30 s after the suction process termination, even by low concentrations that were not visually detectable. According to the manual of the DT-003 tube the final positive colouration has to be created within 1 min after the suction process termination. That means that by tristimulus colourimetry the entire detection procedure could be reduced by 0.5 min. By Dräger and Gastec tubes the measurement confirmed rapid response time according to the respective manual.

Kinetics of colouration change was also studied (Fig. 2). The stability of indication layer colouration came up in the Oritest tube in 90 ± 20 s, in the Dräger tube in 420 ± 20 s, and in the Gastec tube in 120 ± 15 s. The measurement was performed 8 times for each tube. These results represent a 99.73 per cent confidence interval. In the Gastec tube the maximum amplitude was detected immediately, whereas in other tubes the maximum was reached at the end of measurement where a plateau was formed. In the Chlor 0.2/a tube (Dräger), the start-up time seems to be protracted but in recorded intervals (11 s -12 s) the difference between two dE values was less than 1 per cent at 20 s (declared response time).

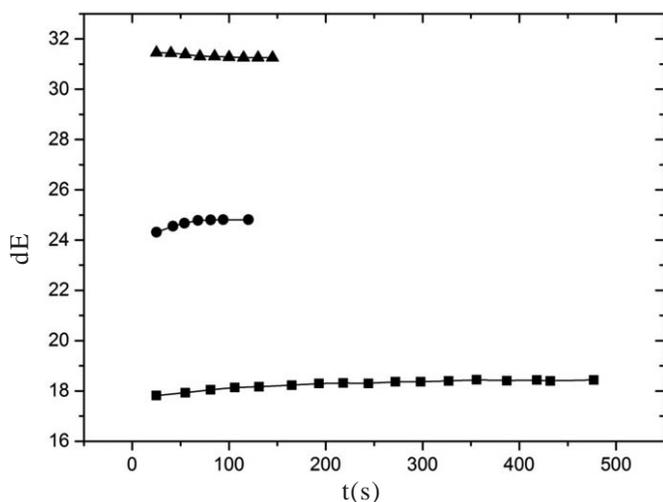


Figure 2. The leading edges of total colour difference (dE) of indication layers of Oritest (●), Dräger (■) and Gastec (▲) tubes for chlorine after suction process termination.

For detection purposes, for indicating a threat of chlorine presence the response time for Oritest, Dräger and Gastec tubes is 30 s, 20 s, and 45 s respectively, using tristimulus colourimetry. For quantitative measurement of chlorine concentration the required waiting period is 90 s, 420 s, and 120 s.

3.2 Limit of Detection

Declared limits of detection were also verified by the devised method. A possible lowering of mentioned parameters of tubes was expected. This was determined using the equation below (S_{LOD} is signal at LOD, S_{std} means signal of standard and σ_{std} is standard deviation of standard; z is factor for selected confidence limit, it was fixed to value of 3, that is valid for significance level $\alpha = 0,00135$). Ascertained results were verified experimentally with chlorine sequentially.

$$S_{LOD} = S_{std} + \sigma_{std} \quad (3)$$

A comparison of measured outcomes and declared limits is demonstrated in Table 2. In the Oritest tube it was confirmed that using the devised objective evaluation method, a 4.3 times lower concentration was reached than the limit of detection. In other tubes, limits were verified while lower concentrations were not caught.

Table 2. Comparison of declared limits of detection (LOD (D)) and limits reached by tristimulus colourimetry (LOD (TC))

Detector tube	Producer	LOD (D) (mg/m ³)	LOD (TC) (mg/m ³)
DT-003	Oritest	3 ¹⁹	0.7
Chlor 0.2/a	Dräger	0.6 ¹⁷	0.6
8H Chlorine	Gastec	16 ¹⁸	15

3.3 Reflectance Curves

Dependence of reflectance (R) on wavelength in the entire visible spectrum – reflectance curve – was also monitored for each tube. There were significant differences between standards and samples curves but the results were not suitable for quantitative measurements. Nevertheless, the reflectance curve is unique for each particular colour and the results are suitable for quality control of respective detector tubes. Reflectance curves of layers before and after colouration changes were different for selected tubes (base curves of Dräger and Gastec tube are merely similar). The reflectance curve depends not just on layer colour but also on sorbent material and its reflective properties, sorbent graininess, case tube material, reagents and their concentration and presence of additive chemicals. Comparison of standard and sample reflectance curves of each tube are expressed in Figs 3-5.

In Table 3 wavelengths with the biggest differences between standard and sample reflectance values are stated. Dräger tube measurement was characterized by the sharpest colour change. From confrontation with kinetic stability data (Fig. 2), an observation arose that layers with larger %R change form colouration stability plateau more slowly.

3.4 Calibration Graphs

For the possibility of quantification of the detection method in Oritest tubes, intervals were searched in which a

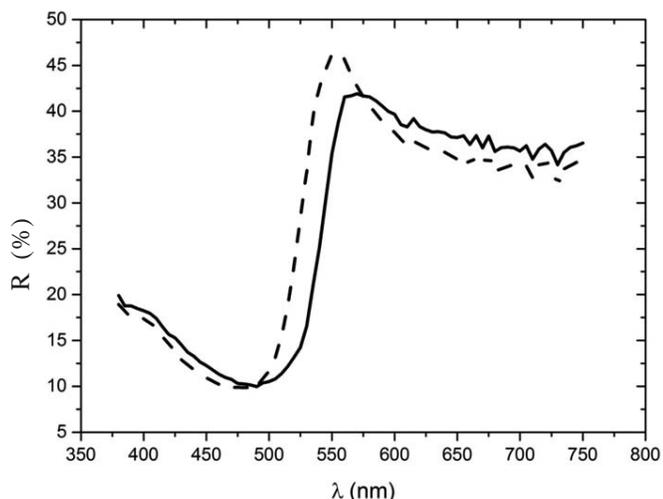


Figure 3. Reflectance curves of Oritest DT-003 tube before (dashed line) and after suction of 9 mg/m³ of chlorine.

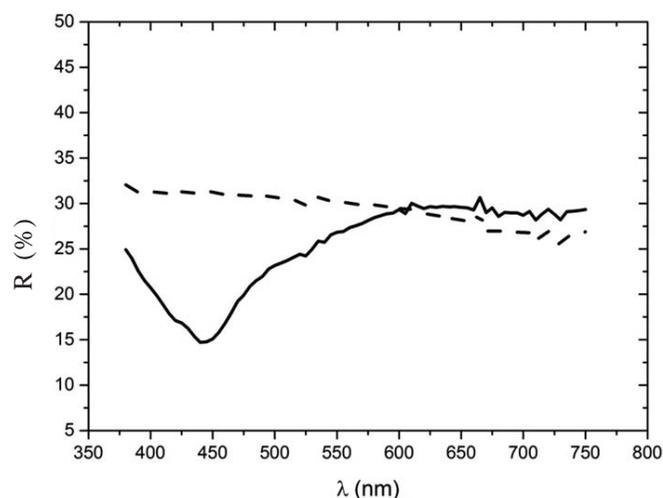


Figure 4. Reflectance curves of Dräger Chlorine 0.2/a tube before (dashed line) and after suction of 10 mg/m³ of chlorine.

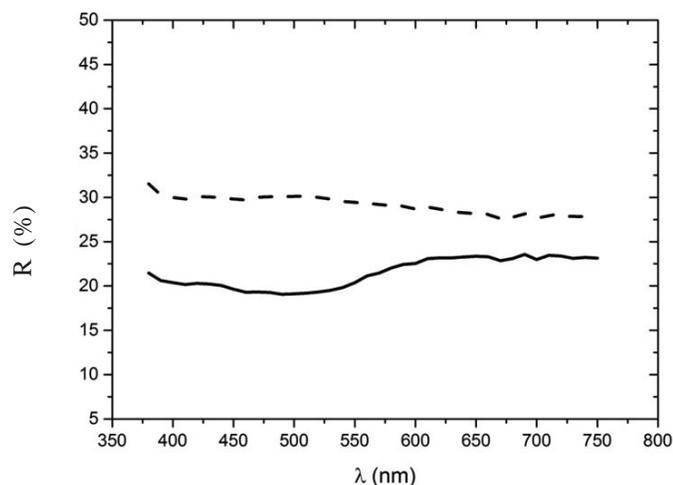


Figure 5. Reflectance curves of Gastec 8H Chlorine tube before (dashed line) and after suction of 10 mg/m³ of chlorine.

Table 3. Wavelengths (λ) with most significant differences between standard and sample reflectance ($\%R_{std}$, $\%R_{sam}$) for compared detector tubes

Detector tube	Producer	λ (nm)	$\%R_{std}$	$\%R_{sam}$
DT-003	Oritest	550	46.21	35.40
Chlor 0.2/a	Dräger	440	32.07	13.83
8H Chlorine	Gastec	435	30.04	19.05

correlation between the total colour difference in the tube and analyte concentration could be mathematically proven. As illustrated in Fig. 6, the linear dependence ranged between 0.7 mg/m³ and 45 mg/m³ with a correlation coefficient of 0.9746. Measurements were performed 8 times for each concentration. Due to a lack of colour homogeneity the relative standard deviation of the total colour difference was up to 30 per cent. Compared to the Dräger tube (15 per cent) and Gastec tube (10 per cent), the outcome is worse, in spite of using the objective evaluation method. The positive here is the fact that although it is not a requirement of the tube, using the devised method we are able to determine the concentration of chlorine in the defined interval.

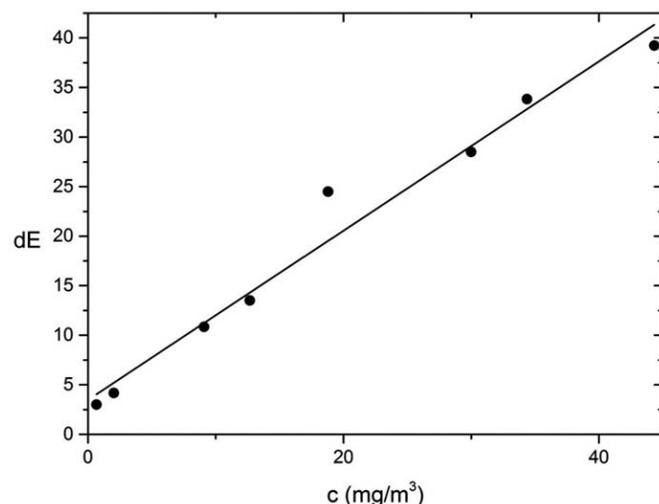


Figure 6. Dependence of total colour difference of Oritest DT-003 detector tube on concentration of chlorine.

4. CONCLUSION

A method for objective evaluation of detector tubes colouration change was devised. An evaluation of an Oritest tube for chlorine detection was performed and comparison with relevant products from Dräger and Gastec manufacturers was carried out. The declared limit of detection of DT-003 is 3 mg/m³. Using tristimulus colourimetry this limit was significantly lowered. For Dräger and Gastec tubes the declared limits were confirmed (0.6 mg/m³ and 16 mg/m³ respectively).

The response time measurement of tubes showed that 25 s after suction process termination, the Oritest tube layer had already performed the relevant response, even in concentrations that were not detected visually. This attribute allows an operator to detect chlorine in 0.5 min using tristimulus colourimetric evaluation. Dräger and Gastec tubes responded immediately.

Stability of colouration study showed that practically all tubes reached stability eventually (in comparison with declared time values for unquestionable visual detection evaluation). The best results were reached by the Oritest tube. Reflectance curves for all tubes were monitored for creating an etalon useful for colour quality control. The larger the reflectance change, the slower the colouration kinetic.

A calibration graph was formed for DT-003. Gastec and Dräger tubes are normally designated for the measuring of chlorine concentration. Using the objective evaluation method, the Oritest tube could measure concentration in an interval between 0.7 mg/m³ and 45 mg/m³.

The outcomes of the research illustrated that, using a tristimulus colourimetry based evaluation device, it is possible to speed up and quantify the detector tubes-based detection system. This method could be applied in military laboratories for quality control of chlorine tubes, even in expired batches. This discovery could also be an initiative for projecting a handheld spectrophotometer that would evaluate a tube's response in field conditions. Reduced response time, a lowered limit of detection and linear dependence between colouration change and concentration could significantly improve field chlorine detection.

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