# Quantification of 4-chloro-3-methylphenol in industrial aqueous effluent by GC-MS

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## Introduction

As endocrine disruptors, chlorophenols can endanger aquatic environments. This is why these pollutants are subject to rigorous controls, especially for industrial wastewaters.
However, it is not advised to analyze them by GC without preparation because of their high polarity which produces a broad tailed peak. It is thus necessary to convert them into a less polar form, for instance by acetylation.
Gas chromatography coupled with mass spectrometry is particularly adapted for the analysis of chlorophenols thanks to its high sensitivity and selectivity.
This article presents how to analyze 4-chloro-3-methylphenol (4C3MP) by GC-MS with preliminary acetylation and use of an internal standard, the 4-bromophenol.

## Experimental conditions

Due to the fact that the samples are contaminated (being really dirty), a purification is needed by changing pH. The 4C3MP has a pKa of 9.55, so nitric acid is added to reduce the pH and to mainly have the molecular form of chlorophenol. Furthermore, it is possible to extract this with toluene. Using a solution of sodium carbonate, it will become more alkaline and water soluble.
Samples are derivatized by acetylation by adding sodium carbonate and anhydrous acetic acid. This step allows the conversion of the alcohol function into acetate. Eventually, an extraction with hexane is carried out to concentrate the acetate of 4-chloro-3-methylphenol (A4C3MP).
During all these steps, the internal standard, 4-bromophenol, is used to follow the evolution of the pollutants studied.
Once the acetylation is performed, it is then possible to analyze it by GC-MS.

## Results and discussion

Before applying the operating procedure on samples, aqueous standards were tested in order to verify that all pollutants had been extracted. Then the sample is purified, the results show losses of 4C3MP with an efficiency of around 30% instead of 95% without purification. So the purification step is deleted.
The chromatogram obtained by GC-MS is shown in figure 2. For each chromatographic peak, a characteristic mass spectrum is associated with a parent ion mass.
The acetate of 4-chloro-3-methylphenol shows its parent ion mass at m/z = 142 and a fragment ion with a high relative abundance at m/z = 107. The fragment ion used for the internal standard appears at m/z = 172 (parent ion). With an internal calibration, it is possible to determine the concentration of the chlorophenol in the industrial effluent.

Fig.1 : Chromatogram after acetylation of 4-chloro-3-methylphenol and the internal standard
Fig.2 : Mass spectrum of 4-chloro-3-methylpenol acetate

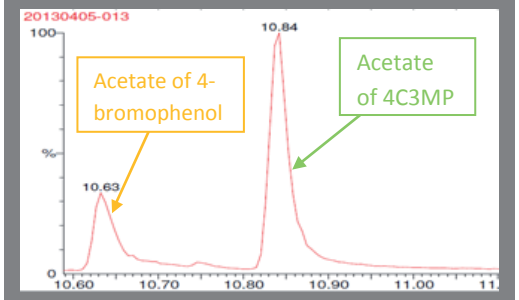


Fig.1

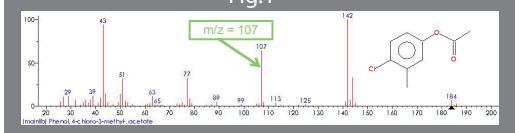


Fig.2

## Conclusion

This procedure allows the quantification of chlorophenols in samples. However, since it is necessary to derivate the pollutants, it would not be advised to perform qualitative analysis. It was observed that the acetylation alters the effluent components. It could be interesting to test another method which would keep the pollutants intact, such as Solid Phase Extraction (SPE).

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