# A cheap and simple passive sampler using silicone rubber for the analysis of surface water by gas chromatography-time of flight mass spectrometry

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## **ABSTRACT**

Water pollution events may arise rapidly, requiring a methodology that is easy to implement, fast to deploy, and sufficiently sensitive to detect the trace presence of hazardous contaminants. A cheap and easy to use silicone rubber (polydimethylsiloxane (PDMS)) miniature passive sampler is described. In order to test the methodology, pollutants were concentrated, in situ, from surface water in and around Pretoria, South Africa. The versatile sampler allowed for conventional and enhanced sensitivity, solvent-free analysis by comprehensive gas chromatography – time of flight mass spectrometry (GCxGC-TOFMS) and high resolution TOFMS (GC-HRT). Contaminants detected in surface water include caffeine, personal care products, pharmaceuticals, pesticides and polycyclic aromatic hydrocarbons.

Keywords: passive sampler, silicone rubber (PDMS) tubing, GCxGC-TOFMS, GC-HRT, surface water quality

### INTRODUCTION

Water supply in South Africa is characterised by both achievements and challenges. In recent years, the country has made satisfactory progress with regard to improving access to water supply in urban areas. However, in some rural areas, women spend up to one-third of their time fetching water, and many rural dwellers are still without access to safe water sources and are compelled to take untreated water from rivers and dams. As a result of this situation, it is necessary to have a methodology which can be used for fast determination of pollutants, both organic and inorganic, which may possibly contaminate streams and wells. As water quality problems can arise very quickly, and can also be extremely short lived (e.g. spills or short- term releases into rivers), the methodology must be easy to implement, rapid to deploy, and must be sufficiently sensitive to detect the trace presence of harmful contaminants.

Spot water sampling gives chemical information specific to the moment of sampling and may fail to detect intermittent or transitory pollution. In contrast, passive sampling delivers a chemical profile representing days, weeks, or months depending on the duration of sampling. Furthermore, passive samplers accumulate analytes over time and thus provide enhanced sensitivity for trace level analytes compared to conventional bottle collection of water.

Silicone rubber (polydimethylsiloxane (PDMS)) functions as a hydrophobic solvent (Baltussen et al., 2002) and is therefore ideally suited for the in situ enrichment of persistent organic pollutants from water. Passive samplers are solvent extracted prior to instrumental analysis to obtain the trapped contaminants in an easily analysable form. Solvent extraction has the

disadvantage that it requires large amounts of often hazardous solvents and only microlitre amounts of the solvent extract are analysed. To address the disadvantages of bulk sample collection followed by solvent extraction, a cheap and easy to use passive sampler made from silicone rubber (PDMS) tubing, previously developed for solvent-free extraction of soil (Naudé et al., 2011; Naudé and Rohwer, 2012), was used. The passive sampler was applied to concentrate pollutants from surface water in and around Pretoria, South Africa. First results are reported.

### **METHODOLOGY**

# Sampling sites

Streams were sampled, in situ, at 3 different locations:

- Site 1: A small stream (Hartbeesspruit) flowing through the University of Pretoria (UP) recreational area, close to sports grounds, recreational braai (barbecue) areas and student residences (for 3 days)
- Site 2: The Moreletaspruit flowing through residential areas (for 3 days)
- Site 3: The Rietvleispruit running through the Rietvlei Nature Reserve (5 weeks).

The watercourses run through natural, industrial, and residential areas, and informal settlements. Sampling was performed from October 2013 to February 2014, in the summer, during the rainy season in Pretoria, South Africa.

# Miniature passive sampler

A sampling loop was fashioned by taking a 10.5 cm (0.02 g) length of silicone elastomer medical grade tubing (0.64 mm OD  $\times$  0.3 mm ID, Sil-Tec Technical Products, Georgia, USA) and joining the ends by inserting a 1 cm piece of fused silica capillary column (250  $\mu m$  ID) (Fig. 1). A loop arrangement prevents water from entering the PDMS tubing and aids ease of

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