## Rapid and Simple Determination of Doxycycline in Water Samples and Honey by $Fe_3O_4$ Magnetic Nanoparticles

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Tetracyclines (TCs) constitute is one of the most important antibiotic families, ranking second in production and usage worldwide [1]. In recent years TCs have been widely used in pharmaceuticals and food additives. The bee-farmers have fed bees with TCs in order to strengthen their resistance to disease but traces of tetracycline would remain in the honey. Therefore, it is important to understand the occurrence, fate and effects, and control of TCs in the environment.

Doxycycline, is one of the kinds of antibiotics of the TC family containing the β-diketonate configuration. Its curative effect is superior to that of TC. Doxycycline hydrochloride (DC), is one of the TC derivations, which has a wide range of antibacterial activity. DC is preferred to other TCs in the treatment of specific infections because of its fairly reliable absorption and its long half-life, which permits less frequent dosage.

It is critical to develop reliable, rapid, precise and economical analytical procedures for monitoring DC that are harmless to the environment as well.

$Fe_3O_4$ magnetite nanoparticles have shown great potential for many nanotechnology applications, including effective adsorbents for removal of undesirable contaminants in water treatment [2]. This nanoadsorbent has a high surface area and a small particle size. In particular, the excellent magnetic property of the powders makes them to be easily recovered by magnetic separation technology after adsorption or regeneration, which overcomes the disadvantage of separation difficulty of common powdered adsorbents [3].

A new spectrometric method is described for the determination of doxycycline (DC) based on $Fe_3O_4$ magnetic nanoparticles. The adsorption characteristics and DC removal efficiency of adsorbents have been determined by investigating the effects of pH, concentration of the DC, amount of adsorbents, contact time, ionic strength and temperature. The mechanism of adsorption was also studied. The adsorption of DC to the $Fe_3O_4$ magnetic nanoparticles could be described by Langmuir-type adsorption isotherms. Short contact time between the reagents, reusability of $Fe_3O_4$ for three times after recycling of the nanoparticles, good precision and accuracy, wide working pH range, and high breakthrough volume are among the highlights of this procedure. The proposed extraction and determination procedure based on magnetic nanoparticles as adsorbent was successfully applied to the determination of DC spiked in honey and various water samples. The proposed method is quick, simple, cheap, and robust, and it does not require the use of organic solvents. Also, the method needs only a magnet and can be performed in any laboratory without sophisticated equipment.

**References**

[1] S. B. Levy, The antibiotic paradox, Perseus Publishing: Cambridge, MA, 2002.
[2] A. Khodabakhshi, M. M. Amin, M. Mozaffari, Iran. J. Environ. Health. Sci. Eng. 8 (2011) 189-200.
[3] J. QU, J. Environ. Sci. 20 (2008) 1-13.

## Solid-phase microextraction based sol–gel technique using poly(ethylene glycol) grafted multi-walled carbon nanotubes as extracting phase

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In this study, poly(ethylene glycol) (PEG) grafted onto multi-walled carbon nanotubes (PEG-g-MWCNTs) were synthesized by the covalent functionalization of MWCNTs with hydroxyl-terminated PEG chains. For the first time, functionalized product of PEG-g-MWCNTs was used as selective extraction phase to prepare the sol–gel solid-phase microextraction (SPME) fiber in combination with gas chromatography-flame ionization detector (GC–FID) for the determination of ultra-trace levels of BTEX compounds, MTBE and non-steroidal anti-inflammatory drugs in real samples. The PEG-g-MWCNTs were characterized by Fourier transform infrared spectra and also thermo-gravimetric analysis, which verified that PEG chains were grafted onto the surface of the MWCNTs. The scanning electron micrographs of the fiber surface revealed a highly porous structure which greatly increases the surface area for PEG-g-MWCNTs sol–gel coating. This fiber demonstrated many inherent advantages, the main being the strong anchoring of the coating to the fused silica resulting from chemical bonding with the silanol groups on the fused-silica fiber surface. The new PEG-g-MWCNTs sol–gel fiber is simple to prepare, robust, with high thermal stability and long lifetime. Important parameters influencing the extraction efficiency such as desorption temperature and time, extraction temperature, extraction time, pH, stirring speed and salt effect were investigated and optimized.

**Keywords:** Solid-phase microextraction; sol–gel technique; Multi-walled carbon nanotubes; Gas chromatography-flame ionization detector.

**References**

[1] A. Sarafraz-Yazdi, A. Amiri, G. Rounaghi, H. Eshtiagh-Hosseini, J. Chromatogr. A 1218 (2011) 5757–5764.
[2] A. Sarafraz-Yazdi, A. Amiri, G. Rounaghi, H. Eshtiagh-Hosseini, Anal. Chim. Acta 720 (2012) 134–141.
[3] A. Sarafraz-Yazdi, A. Amiri, G. Rounaghi, H. Eshtiagh-Hosseini, J. Chromatogr. B 908 (2012) 67–75.
[4] A. Sarafraz-Yazdi, A. Amiri, G. Rounaghi, H. Eshtiagh-Hosseini, Anal. Methods 4 (2012) 3701–3707.

## Colorimetric Sensing of Thionamide anti-thyroid drug Based on the Aggregation of Unmodified Gold Nanoparticles

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When dispersed in liquid media, these nanoparticles exhibit a strong UV–vis extinction band that is not present in the spectrum of the bulk metal. This extinction band results when the incident photon frequency is resonant with the collective excitation of the conduction electrons and is known as the surface plasmon resonance (SPR)[1]. SPR excitation results in wavelength-selective absorption with extremely large molar extinction coefficients (~$3\times1011\ M^{-1}cm-1$)[2]. As a result, gold and silver-based colorimetric detection could provide extremely high sensitivity and allowing sensitive detection of small amounts of analytes.

We report herein the development of a highly sensitive colorimetric method for detection of4-Hydroxy-2-mercapto-6-methylpyrimidine (MZU) which acts as anti-thyroid drug using the citrate capped gold nanoparticles (Au-NPs). This thiol containing molecules exhibit intriguing affinity with Au nanoparticles. The reactivity involves the displacement of the citrate shell by the thiolate shell which is followed by intermolecular electrostatic interactions or hydrogen-bonding between the thiolate shells. The interparticle interactions depends on the ionic strength, pH and Au-NPs concentration of the solution. The interparticle interactions lead to a decrease in the plasmon band at around 521nm and the formation of a new red shifted band. The calibration curve derived from the ratio of changes in the absorption intensity at 650nm for MZU respectively to original wavelength (520 nm). It was linear in the concentration range of $5.0\times10^{-7}$ – $2.75\times10^{-6}$ M . The detection limit (3σ) for MZU was $1.9\times10^{-7}$ M .