The University of Sistan & Baluchestan
Graduate School

The Dissertation of Ph.D. in Analytical Chemistry

Title:

Determination of Cyanide and Simultaneous Analysis of Ascorbic Acid, Dopamine and Uric Acid Using Flow Injection Analysis-Flame Atomic Absorption Spectrometry and Using Electrochemical Method Based on Silver and Silver Hexacyanoferrate Nanoparticles

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Dedicated to:

my wife

my parents

and

everyone who thought me

any things

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Abstract

This dissertation has two parts:

In part I, rapid flow injection–flame atomic absorption spectrometry for cyanide detection is described. Different AgX (X= Cl^-, Br^-, I^- and N_3^-) and Ag_3PO_4 solid-phase reagents (SPR) were tested for indirect determination of cyanide. In a single-line FIA system, the cyanide was allowed to react with AgX SPR, which in turn changed Ag ions in AgX to silver cyanide complexes in a sodium hydroxide carrier stream. The eluent containing the analyte as silver cyanide complexes was measured by FAAS. Variable parameters such as carrier pH, flow rate, loop volume, reactor composition and reactor temperature were optimized. The calibration curves were linear up to 30 and 18 mg L^{-1} with a detection limit of 0.05 and 0.04 mg L^{-1} for AgX and Ag_3PO_4, respectively. The sampling rate and the relative standard deviation were <1.09% and <1.07 and >200 and 220 h^{-1}, for AgX and Ag_3PO_4, respectively. The method was applied to the determination of cyanide in electroplating wastewater.

In part II, Ag and $Ag_4[Fe(CN)_6]$ nanoparticles were synthesized and utilized for detection of cyanide and simultaneous determination of ascorbic acid, dopamine and uric acid.

Silver nanoparticles were prepared and embedded in the three dimensional network of a mercaptopropyltrimethoxysilane (MPS) sol-gel. A clean gold electrode was immersed in a hydrolyzed MPS sol–gel solution containing Ag nanoparticles to assemble three-dimensional silica gel. Thus, modified electrode was prepared to detect cyanide based on the specific reaction of Ag nanoparticle and CN^-. The size of Ag nanoparticles and silica pores was examined by atomic force microscopy and found to be around 34.5 nm and 91.3 nm, respectively.

The performance and factors influencing the performance of the resulting sensor were studied in detail. The detection limit of the sensor was 1.4×10^{-8} mol L^{-1}, and the linear range was from 1.5×10^{-6} to 2.1×10^{-4} mol L^{-1}.

Silver hexacyanoferrate

A silver hexacyanoferrate nanoparticles/carbon nanotubes modified glassy carbon electrode was fabricated and then successfully used for the cyanide determination and simultaneous determination of ascorbic acid, dopamine and uric acid by square wave and cyclic voltammetry. A detailed investigation by transmission electron microscopy (TEM) and electrochemistry was performed in order to elucidate the preparation process and properties of the nanocomposites. The size of silver hexacyanoferrate nanoparticles was determined by TEM around 27 nm. The practical analytical utilities of the modified electrode were demonstrated by the determination of cyanide in industrial wastewater and of ascorbic acid, dopamine and uric acid in urine and human blood serum samples.

Keywords: Flow injection analysis, Solid-phase reactor, Cyanide, Ascorbic acid, Dopamine, Uric acid, Silver and Silverhexacyanoferrate nanoparticles.

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Abbreviations

ΔE_p	Potential peak separation
$\uparrow\Delta I_{pc}$	Increasing in I_{pc}
$\downarrow\Delta I_{pc}$	Decreasing in I_{pc}
A	Surface area of the electrode
AA	Ascorbic acid
AdSV	Adsorptive stripping voltammetry
AFM	Atomic force microscopy
AFM	Atomic force microscopy
AgHCFNPs	Silver hexacyanoferrate nanoparticles
AgNPs	Silver nanoparticles
ATP	Adenosine triphosphate
BBS	Borax buffer solution
BGE	Bare gold electrode
C.S.	Carrier stream
CABS	Chloroacetate buffer solution
CFA	Continuous flow analysis
CGC-ECD	Capillary gas chromatography–electron capture detector
CMCPE	Chemically modified carbon paste electrode
CMEs	Chemically modified electrodes
CNMetHb	Cyanmethemoglobin
CNT	Carbon nanotube
CV	Cyclic voltammetry
CVs	Cyclic voltammograms
D	Dispersion coefficient

DA	Dopamine
DC	Direct current
DDW	Doubly distilled water
DL	Detection limit
F	Faraday constant
FAAS	Flame atomic absorption spectrometry
FIA	Flow injection analysis
GC	Gas chromatography
GC	Glassy carbon electrode
GE	Gold electrode
HC	Holding coil
HPLC	High performance liquid chromatography
HRP	Horseradish peroxidase
IC	Ion chromatography
IgG	Immunoglobulin G
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
ISEs	Ion selective electrodes
LOQ	Limit of quantitation
LRRS	Low – resolution Raman spectroscopy
LRSERS	Low-resolution surface-enhanced Raman scattering
MCEC	Microchip electrochromatography
MHCF	Metal hexacyanoferrate
MPS	Mercaptopropyltrimethoxysilane
MWCNT	Multi-walled carbon nanotube