

## SUPPLEMENTARY DATA

### 1. OPTIMIZATION PARAMETERS CHROMATOGRAPHY

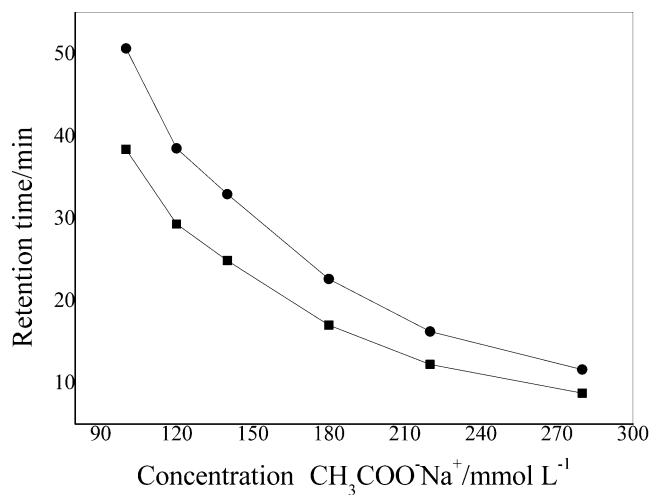


Fig. 1. Effect of the acetate ion concentration at the retention time of the acids (▪) D-galacturonic and (●) D-glucuronic. Flow rate:  $1.0 \text{ ml min}^{-1}$ . Detection potential  $0.45 \text{ V vs. Pd}$ .

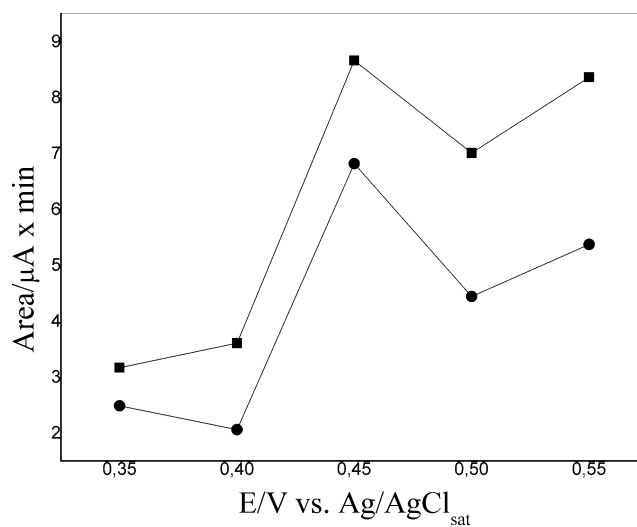


Fig. 2. Variation of applied potential by the peak area in the detection of acids (▪) D-glucuronic and (●) D-galacturonic, on CuNP electrode. Flow rate:  $1.0 \text{ ml min}^{-1}$ . Mobile phase:  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  plus  $280 \text{ mmol L}^{-1} \text{ CH}_3\text{COONa}$ .

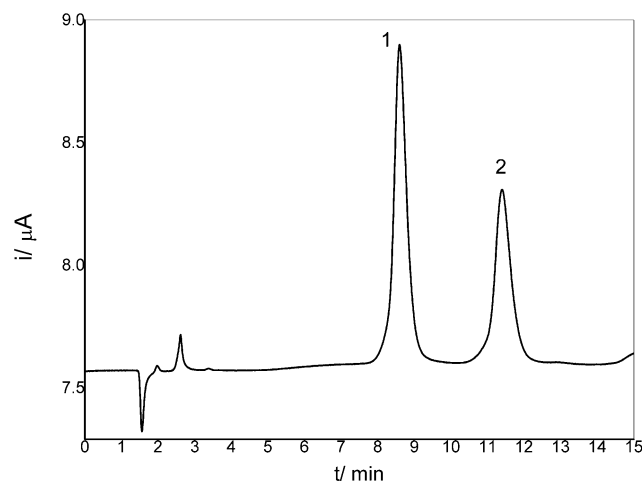


Fig. 3. Chromatogram for the isocratic separation of standard samples (1) D-galacturonic acid, 8.75 min, (2) D-glucuronic acid, 11.56 min. Mobile phase  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  plus  $280 \text{ mmol L}^{-1} \text{ CH}_3\text{COONa}$  with the detection potential of  $0.45 \text{ V}$  vs. Pd and flow rate of  $1.0 \text{ ml min}^{-1}$ .

## 2. CONCENTRATION STUDY OF THE URONIC ACIDS

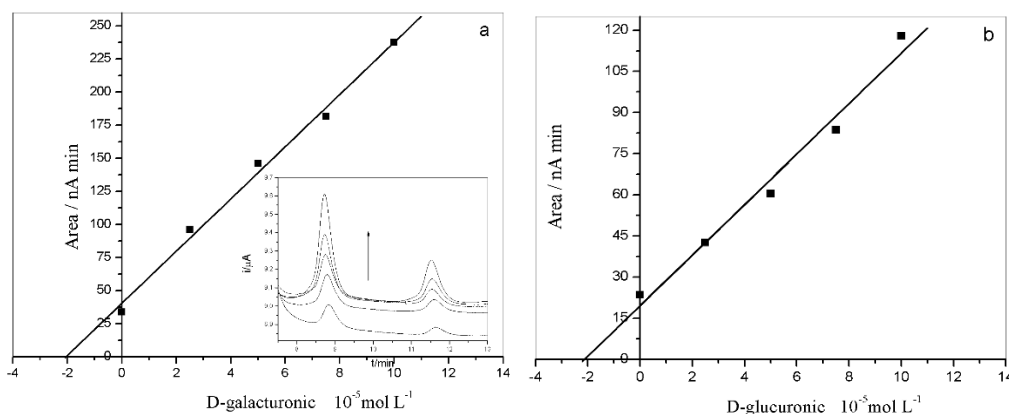


Fig.4. Standard addition method for the acid (a) D-galacturonic and (b) D-glucuronic on CuNP electrode used as amperometric detector in HPLC. Conditions for isocratic separation: Mobile phase of  $0.1 \text{ mol L}^{-1}$  of NaOH with  $0.280 \text{ mol L}^{-1}$  of  $\text{Na}^+\text{CH}_3\text{COO}^-$ , detection potential of  $0.45 \text{ V}$  vs Pd and flow rate of  $1.0 \text{ ml min}^{-1}$

## 3. PROPOSED MECHANISM FOR OXIDATION

In Figure 5, a possible mechanism for the oxidation of uronic acids has been depicted. Owing to the balance of D-glucuronic acid molecule in aqueous solution, at the moment when the ring is open, C-C bonds are broken generating five molecules of formaldehyde and one formic acid molecule. The formaldehyde molecules are subsequently oxidized to formic acid due to the reduction of copper (II) to copper (I) under alkaline conditions ( $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ) on the electrode surface. According to Baldwin and collaborators<sup>1</sup>, ten electrons are found to be transferred in the complete oxidation of D-glucuronic acid using modified electrode with copper (copper film).

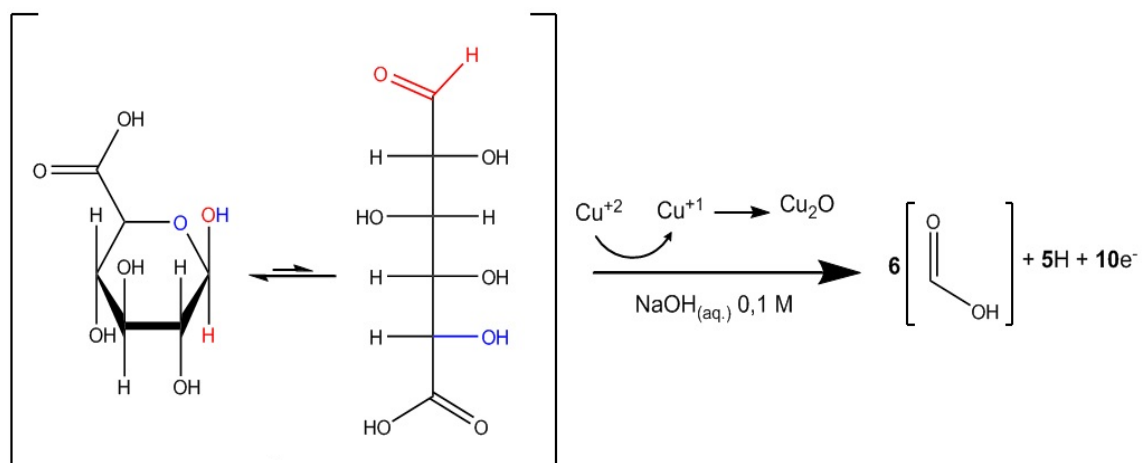


Fig.5. Proposed mechanism for oxidation of D-glucuronic acid using electrode of CuNP.

#### References

- [1] S.V. Prabhu, R.P. Baldwin, *Anal. Chem.*, 1989, 61, 2258-2263.