Supplementary Information

Iodine-starch reaction renewed: Determination of iodate in table salts via the Lab-In-Syringe technique

Cemre Yıldız[1], Ivana H. Šrámková[1], Sercan Yıldırım[2], Petr Solich[1], Burkhard Horstkotte[1,*]

[1] Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové, Charles University, Heyrovského 1203, Hradec Králové, 500 03, Czech Republic

[2] Karadeniz Technical University, Faculty of Pharmacy, Department of Analytical Chemistry, Farabi Street, 61080, Trabzon, Turkey

Content

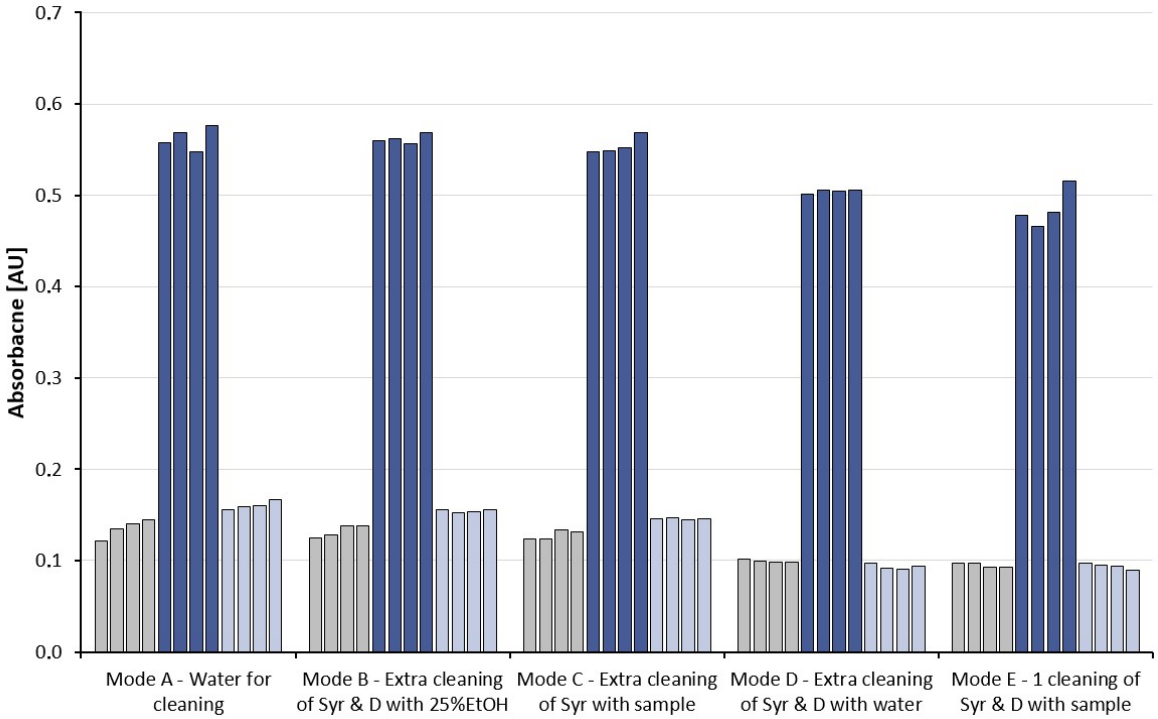


Figure S-1: Effect of cleaning mode on carry over and repeatability evaluated by measuring four times standard solutions prepared with 4 g L^{-1} NaCl containing 2 µmol L^{-1} (grey), 8 µmol L^{-1} (dark blue), and again 2 µmol L^{-1} (light blue) iodate. Syr – syringe, D – detection cell.

25

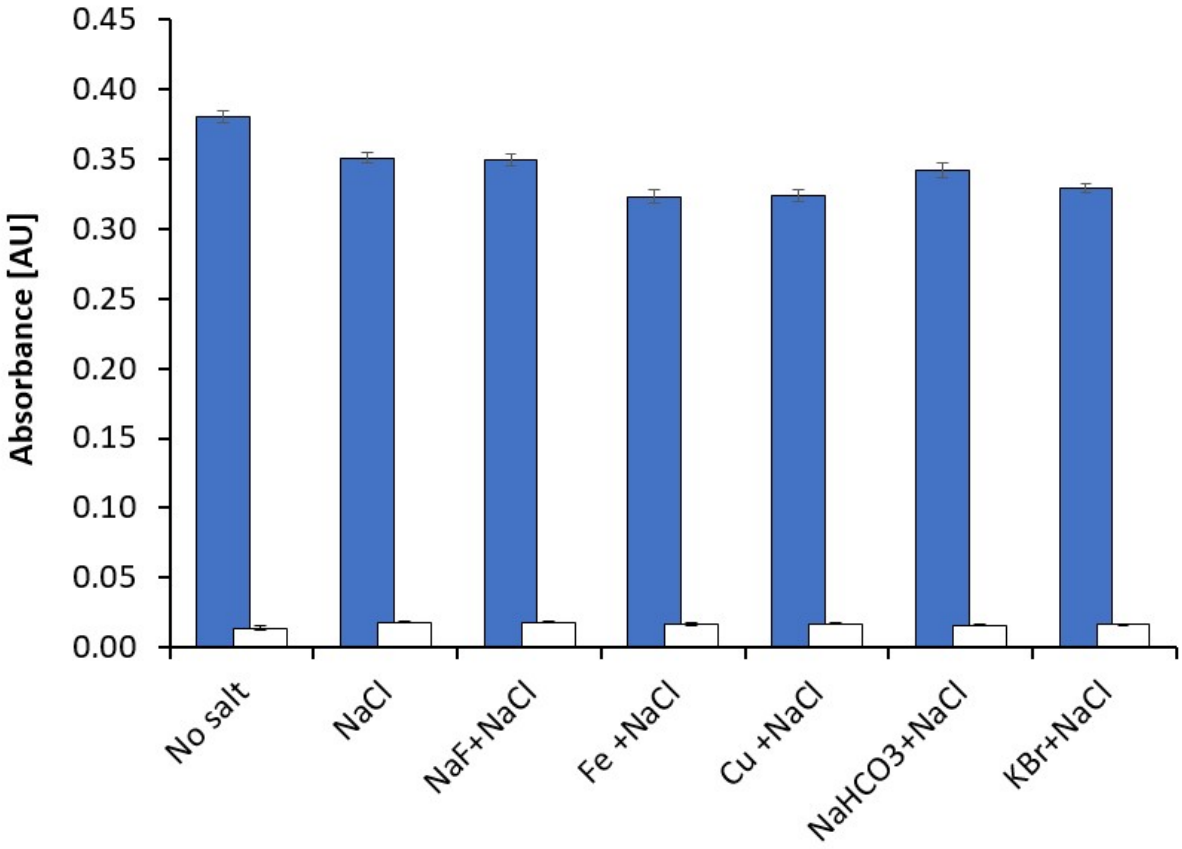
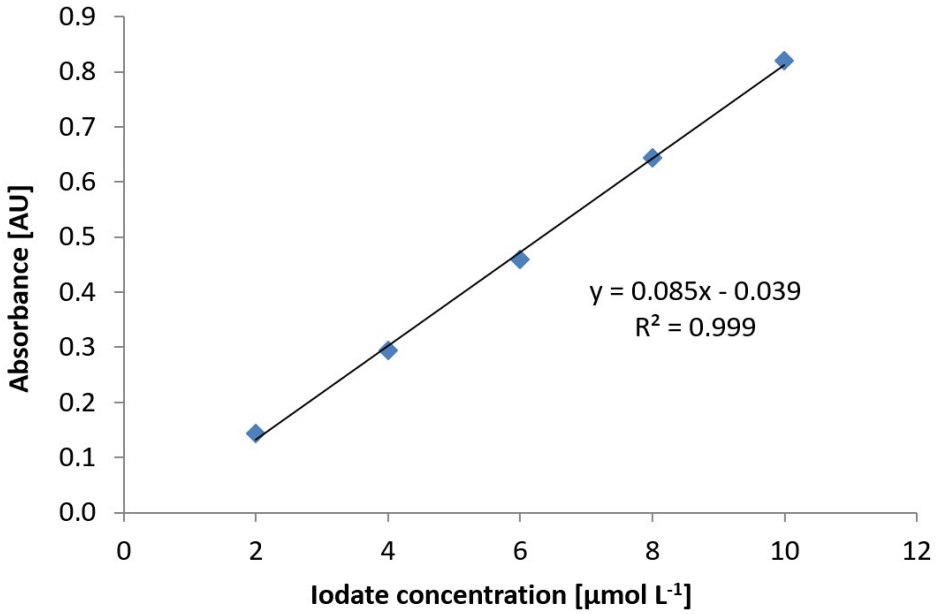


Figure S-2. Evaluation of potential interferents of the optimized method for solutions spiked (blue) with iodate and without iodate (white). Concentrations as given in Table 1.



30

Figure S-3. Exemplary calibration of the developed Lab-In-Syringe methodology for iodate. Conditions: 1 mL iodate standard, 125 µL acidic buffer 500 mmol L^{-1}, pH 0.9, 200 µL iodide 10 mmol L^{-1}, and 100 µL starch solution 0.4 % (w/v), reaction time of 100 s.

Table S-1: Analytical protocol for LIS-automated determination of iodate by iodine-starch reaction.

Step	Instruction	Comment
1	Aspirate 200 µL at 250 µL s^{-1} from HV position 8	Aspirate Air
2	Aspirate 1000 µL from HV position 1 (autosampler) (during method optimization from position 1 or 2 for sample or standard, respectively) Delay (sec) 2	Aspirate Standard or Sample
3	Contact Closure On	Stirring on
4	Aspirate 100 µL at 50 µL s^{-1} from HV position 4 Delay (sec) 3	Aspiration of starch solution
5	Aspirate 200 µL at 250 µL s^{-1} from HV position 5 Delay (sec) 1	Aspiration of potassium iodide solution
6	Aspirate 125 µL at 250 µL s^{-1} from HV position 6 Delay (sec) 3	Aspiration of H_2SO_4 buffer (later, combined starch and acidic buffer solution = 225 µL omitting step 4)
7	Aspirate 50 µL at 250 µL s^{-1} from HV position 8	Aspirate Air to drive all solution into the syringe
8	Delay (sec) 100	Reaction time
9	Contact Closure Off Delay (sec) 2	Stirring off
10	Empty pump at 100 µL s^{-1} to HV position 9 Delay (sec) 5 Start spectrophotometric measurement Delay (sec) 7 Stop spectrophotometric measurement	Emptying syringe to detection cell and measuring after 5 s (to fill the cell) for 7 s (time to pass solution through cell) the absorbance for later averaging

HV: head valve f the syringe pump

Table S-2: Cleaning protocol, here with water.

Step	Instruction	Comment
1	Contact Closure On Aspirate 800 µL at 250 µL s^{-1} from HV position 7	Partially filling the syringe pump with water while stirring
2	Aspirate 500 µL at 250 µL s^{-1} from HV position 8	Aspiration of air
3	Contact Closure Off Empty syringe at 250 µL s^{-1} to HV position 9	Deactivation of in-syringe stirring and emptying syringe to Waste

Table S-3: Greenness evaluation according to AGREE*

1. Off-line analysis
   (generally imperative for a solid sample, therefore a factor weight reduction to 1)
2. 1 g for preparation of 20 mL sample solution
3. On-line placement of analytical device (reaction preparation and detection in one system)
4. Three or fewer preparation steps
5. Automated approach, sample preparation not needed else than dissolution
6. Sulfuric acid and potassium iodide in very small quantities (miniaturized procedure), therefore, factor weight reduction to 1
7. Waste ca 4 mL, mostly water
8. 1 analyte analyzed per time, 13/h, increasable to 20 h^{-1}
9. No energy-intensive detection techniques used, power consumption < 10 Wh per analysis
10. Some reagents are biobased (starch)
11. Toxic reagents used in smallest quantities (H_2SO_4, potassium iodide, < 0.04 g per analysis)
12. No environmental threats by reaction waste nor for operator's safety
    (automated, capsuled) apart from diluted acid (corrosive)

* F. Pena-Pereira, W. Wojnowski and M. Tobiszewski, Anal. Chem., 2020, 92, 10076–10082. doi.org/10.1021/acs.analchem.0c01887