Acetylsalicylic acid (ASA, aspirin) belongs to nonsteroidal anti-inflammatory drugs like ibuprofen or paracetamol that are very popular for treatment of pain and fever. However, aspirin is also used for prevention of heart attack, stroke and also its application—in prevention of colorectal cancer appears-promising. ASA is poorly soluble in water thereby increasing the risk of damage to the gastric mucosa. This promotes a detailed screening for better soluble physical (polymorphs) and chemical (salts, co-crystals) forms of aspirin. Many patents are focused on the preparation of the sodium aspirin (sodium acetylsalicylate - SAS). Two forms are described – SAS dihydrate and anhydrate. Surprisingly, no structure of SAS has been solved yet. Preparation of a salt is a complicated procedure. A tiny amount of water is added to the reaction between aspirin and sodium bicarbonate. While the presence of water is essential to drive the reaction, it promotes ester hydrolysis of the resulting salt as well. That renders the preparation of SAS highly unreliable, with poor reproducibility. Nevertheless, we successfully managed to prepare single-crystals of SAS - dihydrate and anhydrate and optimized their preparation. Furthermore, a new form of SAS was discovered - SAS monohydrate. All structures were determined by single-crystal diffraction. The-SAS dihydrate was later dehydrated to SAS anhydrate. The dehydration was studied by thermoanalytical methods (TGA/DSC). Hydrates were not stable in the air and hydrolyzed to sodium salicylate within few hours. This work was supported by the Grant Agency of Czech Republic, Grant no. 206/16/10035S.