A novel bead injection (BI) extraction chromatographic microflow system exploiting high-capacity lab-on-valve (LOV) platform coupled with inductively coupled plasma mass spectrometric detection is developed for rapid and automated determination of plutonium in human urine. A microconduit (1 mL) incorporated within the LOV processing unit is loaded on-line with a metered amount of disposable extraction chromatographic resin (up to 330 mg of TEVA) through programmable beads transport. Selective capture and purification of plutonium onto the resin beads is then performed by pressure driven flow after preliminary sample pretreatment. The analytical results demonstrate the large capacity of bead surfaces for uptake of Pu within the tailor-made LOV platform that fosters processing of large-sized biological samples, e.g. 1 L of human urine, along with good reproducibility for automatic column renewal (0.319 ± 0.004 g, n=5). The chemical yields of plutonium were averagely better than 90% under the optimal experimental conditions and the entire analytical procedure could be accomplished within a short timeframe (<3 h) as compared to manual counterparts (1-2 days). Therefore, the developed system is well suited for expedient analysis of low-level plutonium in urine of exposed individuals as required in emergency situations.