We prove $S \cup \{\vec{w}\}$ is linearly dependent. We assume without loss of generality that there is no zero vector in S, for otherwise a zero vector will automatically make this set linear dependent. Since $\vec{w} \in \operatorname{span}(S)$, by the definition of span, we can find coefficients $c_1, \dots, c_k$ in $\mathbb{F}$ such that

$$\vec{w} = c_1\overrightarrow{v_1} + \cdots + c_k\overrightarrow{v_k}$$

which is equivalent to

$$0 = c_1\overrightarrow{v_1} + \cdots + c_k\overrightarrow{v_k} - \vec{w}$$

Since the coefficient of $\vec{w}$ is -1, which is non-zero, we know from the definition of linear dependency that $S \cup \{\vec{w}\}$ is linearly dependent